

Technical University of Denmark



## Characterization of leaching from waste incineration air-pollution-control residues

Astrup, Thomas Fruergaard; Christensen, Thomas Højlund

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# Characterization of Leaching from Waste Incineration Air-Pollution-Control Residues

Thomas Astrup



Characterization of Leaching from  
Waste Incineration Air-Pollution-Control  
Residues

Thomas Astrup

Ph.D. Thesis

March 2004

Environment & Resources DTU  
Technical University of Denmark

***Characterization of Leaching from Waste Incineration  
Air-Pollution-Control Residues***

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Environment & Resources DTU  
Library  
Bygningstorvet, Building 115, Technical University of Denmark  
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(+45) 45 25 16 00  
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# Preface

This Ph.D. thesis has been made in collaboration between Environment & Resources DTU at Technical University of Denmark and Center for Waste Research at DHI - Water and Environment. The work was funded jointly by the Danish Research Agency, the Center for Waste Research and the Technical University of Denmark. Professor Dr. Agro. Thomas H. Christensen and Chief Engineer Ole Hjelmær served as supervisors. The contributions to the literature originating from this Ph.D. work are summarized below.

- I) Geochemical modeling of leaching from MSWI air-pollution-control residues by Astrup, T.; Dijkstra, J.J.; Comans, R.N.J.; van der Sloot, H.A.; Christensen, T.H. Submitted to *Environ. Sci. Technol.*
- II) Characterization of MSWI residues with respect to long-term pH development by Astrup, T.; Jakobsen, R.; Hansen, J.B.; Hjelmær, O.; Christensen, T.H. *Manuscript.*
- III) Estimation of long-term leaching from waste incineration air-pollution-control residues by Astrup, T.; Mosbæk, H.; Christensen, T.H. Submitted to *Waste Manage.*
- IV) Chromium release from waste incineration air-pollution-control residues by Astrup, T.; Rosenblad, C.; Trapp, S.; Christensen, T.H. *Environ. Sci. Technol.*, 39, 3321-3329.

The above articles are not included in this www-version of the thesis, but they can be obtained from the Library at Environment & Resources DTU, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Lyngby (library@er.dtu.dk). The articles are referred to by their roman numerals. In addition to these articles, six extended abstracts for international conferences and one journal article have been published partly or fully based on this thesis.

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Copenhagen, March 2004.

Thomas Astrup

# Summary

Waste incineration generates solid residues with high contents of salts and heavy metals that may leach to the surrounding environment upon disposal. Residues from flue gas cleaning, i.e. air-pollution-control (APC) residues, are highly alkaline and have potentials for leaching in very long periods of time. This leaching needs to be quantified and evaluated in a long-term perspective in order to manage the residues in a sustainable manner, however the time frames involved render this unfeasible using traditional leaching tests. This thesis provides a methodology for estimating long-term leaching from APC residues.

A relation between pH of a residue leaching system and the liquid-to-solid (L/S) ratio can be produced based on data for leaching of alkalinity as a function of pH. By relating alkalinity leaching at specified pH-values to losses in residue alkalinity, it is possible by a simple mass balance approach to associate pH of a leaching system with the L/S ratio. This may further be combined with relationships between metal leaching and pH to provide estimated leaching as a function of L/S until depletion from the solid phase.

Typically, APC residues have natural pH-values of 11-12.5 and may maintain alkaline pH-levels for L/S ratios above 2000 l/kg. For a typical landfill, this corresponds to about 100,000 years. This means that metal leaching is most important with respect to high pH. Elements like Ca, Cl, K, Na, Pb and S typically leach in very high concentrations at low L/S, i.e. in mg/l and g/l. Although leaching may continue for very long time, concentrations generally decrease significantly compared to the initial level. Within L/S 5000 l/kg, only Al, Mg and Zn are predicted to have higher leachate concentrations than what can be observed at L/S 2-10 l/kg. Uptake of atmospheric CO<sub>2</sub> may somewhat increase the leaching of Ca and S. These two elements can be completely removed from the solid phase within L/S 300-800 l/kg, whereas other elements generally require leaching for more than L/S 2000 l/kg to remove about 20-30 % of the solid content.

In a long-term perspective, leaching of most elements can be considered controlled by mineral solubility, however, specific elements such as Cr may possibly be affected by other mechanisms. In batch leaching experiments, Cr is highly affected by the redox conditions of the test and reaction kinetics. Cr(VI) reduction capacity provided by Al(0) in the residues may significantly lower Cr concentrations within a few hours of experiment, whereas Cr(VI) dissolution may require a day to complete. Al-O<sub>2</sub>-Cr interactions appear to control the release of Cr in batch experiments.





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- I) Geochemical modeling of leaching from MSWI air-pollution-control residues by Astrup, T.; Dijkstra, J.J.; Comans, R.N.J.; van der Sloot, H.A.; Christensen, T.H. Submitted to *Environ. Sci. Technol.*
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# 1. Introduction

Modern lifestyle results in large quantities of solid waste generated every year. In Europe, more than 200 million ton is generated annually from households, companies and public institutions, and collected as municipal solid waste (Eurostat, 2003). Today, about 18 % (corresponding to about 38 million ton) of this waste is incinerated. In order to reduce the amounts of organic waste being landfilled, as required by the EU Landfill Directive (CEC, 1999), increasing amounts of municipal solid waste are likely to be incinerated in Europe in the coming decades.

The main advantages of waste incineration are the significant reductions in weight and volume of the treated waste, and the possibility of utilizing the energy of the waste. The disadvantage of waste incineration is the generation of emissions. While the gaseous emissions from waste incinerators are controlled by increasingly sophisticated technologies for cleaning the flue gas, the retained contaminants are becoming increasingly complex. These solid residues from flue gas cleaning, here termed as air-pollution-control (APC) residues, contain all particles and contaminants not otherwise released to the atmosphere. Due to increasing restrictions on air emissions from European waste incinerators (CEC, 1996; CEC, 2001), it is likely that the amounts of APC residues will further increase from the present level of about 1 million ton annually (ISWA, 2003).

The physical and chemical properties of APC residues render these residues unsuitable for direct reutilization (IAWG, 1997). Consequently, the only presently available disposal option for APC residues is landfilling, with or without utilization (for details see ISWA, 2003). The main environmental concern related to landfilling of incineration residues is the release of contaminants by leaching. APC residues contain high levels of soluble salts and heavy metals, and have potential for leaching in high concentrations, e.g. typically up to about 10-100 g/l, of Ca, Cl, K, Na and Pb, and probably for a long time (Hjelmar, 1996; IAWG, 1997). In addition, leaching of organic pollutants such as dioxins has been discussed, however this is generally not considered a major concern with respect to APC residues, as these compounds are strongly bound to the residue matrix (McKay, 2002).

Sustainable management of APC residues requires that the leaching potential is assessed and properly addressed in order to avoid short and long-term impacts on the environment, and to avoid the need for prolonged periods of active measures for leaching control. Ultimately, the leaching from landfilled APC

residues should be assessed in the entire period in which the landfill exists, i.e. in periods with active operation and periods thereafter.

The potential leaching from APC residues is traditionally assessed by performing one or more leaching tests, i.e. experiments in which a volume of water is brought into contact with a specified mass of residue (IAWG, 1997), and then relating the leaching to the liquid-to-solid (L/S) ratio of the test. This L/S ratio can further be related to a landfill leaching scenario with rainwater infiltrating the residue body and thereby increasing the L/S ratio. Real-life leachate concentrations may be assessed by column and lysimeter experiments within an L/S ratio of about 10 l/kg, but at much higher L/S ratios these methods are not practical due to time requirements. Batch experiments may provide means to evaluate leaching at somewhat higher L/S ratios, for example L/S 100 l/kg. However, as batch experiments average the leaching over the L/S ratio used in the test, batch leaching tests at high L/S will not provide detailed information about real-life leachate composition. Leaching at very high L/S, or for very long periods, may only be assessed by modeling (Hellweg, 2000). This requires, however, that the chemical composition of the residues and the geochemical properties of the leaching system are well understood. Additionally, modeling requires that the possible effects on leaching from long-term weathering reactions are considered. Presently, this is not the case. A number of studies have reported geochemical properties of treated APC residues, however these properties are specific to the individual treatment technologies (e.g. Eighmy et al., 1997; Ludwig et al., 2000; Baur et al., 2001) and are not generally applicable to other treatment or disposal options. Although a few studies have included geochemical modeling on leaching from untreated APC residues (Gardner, K., 1991; Eighmy et al., 1995; van Herck et al., 2000), no detailed investigation has been performed with a long-term perspective in mind.

The leaching potential of a residue is often determined by batch tests at high L/S and low pH, e.g. the availability test performed in two steps of L/S 100 l/kg with pH-values of 7 and 4, respectively (Nordtest, 1995; NNI, 1994; Fällman, 1997). Presently, there is no method for relating this potential leachability to the L/S ratio of an actual leaching system, i.e. a disposal site, because the leaching data obtained do not reflect the L/S ratio of the test. This means that although an operationally defined quantification of the leachability can be obtained, the leachability is not applicable in the context of assessing future environmental impacts as the data cannot be related to time or L/S. Further, there is no method available for assessing the leachate concentrations or the leaching system pH at L/S ratios not covered by experimental data.

With the intention of improving the basis for performing environmental impact assessments on APC residue disposal options, the aim of this thesis is to:

- i) Investigate the potential changes in the pH of leaching systems, and relate these pH changes to the liquid-to-solid (L/S) ratio of the leaching system.

- ii) Determine possible controlling factors on the leaching of important inorganic pollutants.
- iii) Evaluate the potential effects on pH and leaching from weathering reactions related to uptake of CO<sub>2</sub> from the atmosphere.
- iv) Based on the above provide a method for estimating leachate concentration levels and depletion rates of elements from the solid residues, with a focus of relating this information to the L/S ratio of a leaching system in a long-term perspective.

The above issues are discussed only with respect to APC residues in granular form, and although the work provides a basis for improving and understanding the processes related to residue stabilization, chemical or with hydraulic binders, the focus is placed on the untreated APC residues in order to provide a more generic outcome. Unless otherwise stated, the term "APC residues" covers non-stabilized residues only. For detailed information about APC residue stabilization and leaching from stabilized residues, please refer to (IAWG, 1997; Eighmy et al., 1997; Ludwig et al., 2000; Baur et al., 2001; Hjelmar et al., 2001; Sørensen, 2001; van der Sloot et al., 2001; Lundtorp et al., 2002; Jensen et al., 2002; ISWA, 2003).



## **2. Waste Incineration Air-Pollution-Control Residues**

### **2.1 Introduction**

Waste incineration generates a number of solid and liquid effluents in addition to the gaseous emissions. The solid residues include bottom ash, which primarily consists of coarse non-combustible materials and unburned organic matter, collected at the end of the grate in the furnace. Grate siftings have similar characteristics as bottom ash and are particles that fall through the openings in the grate. Typically, bottom ash and grate siftings are combined into one residue, corresponding to about 20-30 % by weight of the waste input. Smaller grained-sized particles are transported away from the grate and furnace chamber by the flue gas. The coarse fraction of these ashes is immobilized and removed from the flue gas in the boiler system, termed boiler ash, and the fine fraction is removed in subsequent filters, and is termed fly ash. The boiler ash is often combined with the bottom ash. Grate siftings, bottom ash and boiler ash will not be discussed further. Air-pollution-control (APC) residues are formed as reaction products from neutralization of acidic components in the flue gas, i.e. HCl, HF and SO<sub>2</sub>, and may be in solid form or as sludge depending on the flue gas cleaning technology used, see description later. In practice, these reaction products are most often combined with the fly ashes, thus constituting a single residue output corresponding to about 2-5 % by weight of the waste input. In this work, air-pollution-control residues are defined to include all solid residues produced after the heat recovery system.

In this chapter, the major types of APC residues are briefly outlined, and the general characteristics of the residues are discussed with focus on chemical properties as well as residue mineralogy.

### **2.2 Types of APC residues**

The three main types of flue gas cleaning technologies used in waste incineration are dry systems, semi-dry systems, and wet systems (IAWG, 1997).

In dry and semi-dry flue gas cleaning systems, slaked lime is injected into the flue gas in order to neutralize the acidic components. Dry systems inject the lime in a dry form, whereas the semi-dry systems inject lime as slurry. The main differences with respect to the residues are the better possibilities of optimizing the amount of lime used in semi-dry systems compared with dry systems. Usually



the lime injection is done before fly ash is removed from the flue gas. Thus, APC residues from dry and semi-dry systems usually include fly ash, reaction products from neutralization reactions between the injected lime and components in the flue gas, as well as unreacted lime. The amount of unreacted lime in residues from dry systems is often higher than in residues from semi-dry systems. In some incinerators, activated carbon is injected in the flue gas for removal of dioxins. This is in some cases done before the fly ash is removed, usually by fabric filters but also electrostatic precipitators are used.

In wet flue gas cleaning systems, the fly ash is removed before neutralizing the acidic components, thereby allowing the fly ash to be separated from the reaction products. After removal of the fly ash, the flue gas is washed with water. Several washing steps may be included; in this case, the first step is for removal of HCl and HF and the following is for removal of SO<sub>2</sub>. The pH of the wastewater from the first step is below zero, and the water is treated in order to increase pH to neutral and to precipitate heavy metals. Sludge is produced from this treatment and is in some cases mixed with fly ashes to produce a single residue. Wastewater from a second washing step is oxidized and treated with Ca in order to precipitate gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). Sludge and gypsum are not discussed further in this work.

The chapters 2, 3 and 4 focus on APC residue samples from a semi-dry flue gas cleaning system and fly ash samples from an incinerator equipped with a wet flue gas cleaning system. The semi-dry (SD) residue contains activated carbon and was captured by fabric filters, while the fly ash (FA) was captured in an electrostatic precipitator. Chapter 5 discusses experiments including APC residues from incinerators with dry, semi-dry and wet flue gas cleaning technologies.

## 2.3 Main characteristics

### *Chemical characteristics*

The semi-dry residue (SD) and the fly ash (FA) both contain fly ash but the semi-dry residue additionally contains reaction products and excess lime. Both residues are very fine-grained with a grey color, the FA residue somewhat darker than the SD residue. Table 1 lists the chemical composition of the SD and FA residues. As fly ash is the main constituent of the semi-dry residue, about 90 % by weight (IAWG, 1997), the two residues to a certain extent share similar characteristics.

The heavy metals volatilized during incineration are condensed on particles in the flue gas, i.e. mainly fly ash particles, as the temperature decreases in the heat recovery system. The heavy metals are thus mainly associated with fly ash particles, although some level of metal condensation also occurs on the surface of lime particles in semi-dry flue gas cleaning systems (IAWG, 1997).

In semi-dry systems, extra mass is added in the form of lime thereby "diluting" the fly ash. Thus, concentrations of some heavy metals in semi-dry residue may be lower than compared with fly ashes (Table 1). On the other hand, the concentrations of Cl and Ca may be higher as the reaction products from neutralizing HCl are included whereas this is not the case in the fly ash. As

**Table 1.** Solid contents of semi-dry residue and fly ash as determined by acid digestion using HCl, HF and HNO<sub>3</sub> (data from Lundtorp et al., 2002). Also listed are typical concentrations found in APC residues worldwide (data from IAWG, 1997).

		Semi-dry (SD)		Fly Ash (FA)	
		This study	Range	This study	Range
Al	g/kg	30	15-29	60	59-81
Ca	g/kg	250	180-280	200	95-120
Cl	g/kg	140	91-220	60	40-102
Fe	g/kg	10	11-63	20	18-33
K	g/kg	30	15-31	40	30-41
Mg	g/kg	10	7-12	20	14-17
Na	g/kg	30	12-20	40	23-38
P	g/kg	4	-	9	-
Pb	g/kg	5	4-6	7	6-15
S	g/kg	30	8-21	30	21-33
Ti	g/kg	6	3-4	10	8-9
Si	g/kg	70	51-92	100	130-180
Zn	g/kg	20	12-18	20	16-35
As	mg/kg	200	120-210	150	49-200
Ba	mg/kg	750	320-660	1100	940-2600
Cd	mg/kg	210	190-360	280	240-480
Co	mg/kg	10	6-15	20	30-69
Cr	mg/kg	340	110-220	730	430-840
Cu	mg/kg	980	490-860	1600	930-1300
Hg	mg/kg	10	8-18	2	2-10
Mn	mg/kg	500	280-680	900	1000-1600
Mo	mg/kg	10	11-20	30	25-37
Ni	mg/kg	50	23-60	100	91-110
Sr	mg/kg	380	400-500	450	140-400
V	mg/kg	20	19-50	30	32-63

municipal solid waste consists of a very large number of components with an almost unlimited number of chemical compounds, APC residues contain practically every element and have a very complex composition.

The composition of the residues is the result of a large number of processes and factors characteristic for the individual incinerator, most important is the waste input as well as the design and operation of the incinerator, boiler system and flue gas cleaning system. With all these possible variables in mind, APC residues are remarkably similar with respect to the chemical composition. Typically, element concentrations in APC residues from different incinerators fall within one order of magnitude, see Table 1.

**Box 2.1.** Brief overview of the analytical techniques used most often for identification of mineral phases in APC residues (e.g. Kirby and Rimstidt, 1993; Eighmy et al., 1995; Eighmy et al., 1997; IAWG, 1997; Forestier and Libourel, 1998; Enders and Spiegel, 1999).

**XRD.** The most important and widely used technique is X-Ray Diffraction (XRD). This technique provides information about the mineralogy of crystalline phases in the bulk of the residues sample. Amorphous phases cannot be identified by XRD.

**SEM/EDS.** Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS) provides an image of the sample, either as powder, or embedded in epoxy and polished to expose a section of the sample. EDS gives information on the elemental composition of individual particles or minerals, or the composition averaged over a larger section of the sample.

**STEM/XRM.** Scanning Transmission Electron Microscopy (STEM)/X-Ray Microprobe Analysis (XRM) are often used to characterize discrete particles with respect to morphology and elemental composition. The width of the excitation beam is smaller than with SEM, thus higher resolution can be obtained here.

**XPS.** X-ray Photoelectron Spectroscopy (XPS) is a near-surface sensitive technique providing information about the binding environment of elements within the top atomic layers. This technique may enable speciation of redox sensitive elements.

**AES.** Auger Electron Spectroscopy (AES) can be used to obtain information of elemental composition as well as spatial distribution of elements in the near surface of a sample.

**SIMS.** Secondary Ion Mass Spectroscopy (SIMS) is surface sensitive technique with a very high resolution for element quantification. Information about the spatial distribution of elements may also be obtained.

### *Mineralogical characteristics*

The relatively low concentrations of most heavy metals and the complex mineralogy make it difficult to positively identify the solid phases with these elements using analytical techniques such as XRD, see Box 2.1. In contrast, several minerals containing major elements like Ca, S and Al have been identified in APC residues (e.g. Kirby and Rimstidt, 1993; Eighmy et al., 1995; Forestier and Libourel, 1998). Some studies have attempted to improve the possibilities of identifying mineral phases present at low concentrations by fractionating the residue samples before analysis, e.g. with respect to grain size, density, magnetic properties and water solubility (Eighmy et al., 1995; Forestier and Libourel, 1998; Fermo et al., 2000). This appears to significantly improve the resolution compared with studies on bulk samples (Ontiveros et al., 1989; Graydon and Kirk, 1992;

**Table 2.** Summary of mineral phases commonly identified in non-stabilized APC residues.

Formula	Mineral name	Investigations	References
Ca(OH) <sub>2</sub>	Portlandite	b, d, e, j	a) Kirby and Rimstidt (1993)
CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	Anorthite	c, e	b) Kirby and Rimstidt (1994)
CaCl <sub>2</sub>	Hydrophilite	c, j	c) Eighmy et al. (1995)
CaCO <sub>3</sub>	Calcite	a, c, d, e, h, j	d) Alba et al. (1997)
CaF <sub>2</sub>	Fluorite	c, e	e) Forestier and Libourel (1998)
CaSiO <sub>3</sub>	Wollastonite	c, e	f) Enders and Spiegel (1999)
CaSO <sub>4</sub>	Anhydrite	a, c, d, e, f, h, j	g) Fermo et al. (1999)
CaSO <sub>4</sub> ·0.5H <sub>2</sub> O	Bassanite	d, h	h) Fermo et al. (2000)
CaSO <sub>4</sub> ·2H <sub>2</sub> O	Gypsum	a, b, c, e, h	i) van Herck et al. (2000)
Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	Gehlenite	d, j	j) Shimaoka et al. (2002)
Ca <sub>2</sub> SiO <sub>4</sub>	Larnite	d, e	
Ca <sub>6</sub> Al <sub>2</sub> (OH) <sub>12</sub> (SO <sub>4</sub> ) <sub>3</sub> ·26H <sub>2</sub> O	Ettringite	e, g	
CdCO <sub>3</sub>	Otavite	c, i	
Fe(0)	Metallic iron	d, e	
Fe(OH) <sub>3</sub>	Fe(OH) <sub>3</sub> (am)	b, c	
Fe <sub>2</sub> O <sub>3</sub>	Hematite	a, e, f, j	
KCl	Sylvite	a, d, e, j	
NaCl	Halite	a, c, d, c, e, h, j	
PbCl <sub>2</sub>	Cotunnite	b, c, e, j	
PbCO <sub>3</sub>	Cerussite	b, c	
PbO	Massicot	c, e	
PbSO <sub>4</sub>	Anglesite	b, c	
SiO <sub>2</sub>	Quartz	a, c, d, e, f	
TiO <sub>2</sub>	Rutile	a, e	
Zn(0)	Metallic zinc	c, e	
ZnCl <sub>2</sub>	Zinc Chloride	c, e	
ZnCO <sub>3</sub>	Smithsonite	c, i	

Stuart and Kosson, 1994; Alba et al., 1997; Enders and Spiegel, 1999). Table 2 summarizes the most commonly identified mineral phases in APC residues.

The above-mentioned investigations have collectively suggested more than 100 mineral phases to exist in APC residues. About a quarter of these minerals have been identified in two or more investigations (Table 2), indicating that these minerals may be more likely to exist in APC residues in general. The number of investigations, which have identified specific minerals, also indicates the relative abundance of these minerals in residue samples. For example, CaSO<sub>4</sub> phases, halite (NaCl), sylvite (KCl), calcite (CaCO<sub>3</sub>), and quartz (SiO<sub>2</sub>) are reported by several investigations (Table 2) indicating that these minerals are present in high concentrations. However, minerals like gibbsite (Al(OH)<sub>3</sub>), barite (BaSO<sub>4</sub>), hydrophilite (CaCl<sub>2</sub>), magnesite (MgCO<sub>3</sub>) and zincite (ZnO) may also be important although these minerals are only found in one of the above studies. Complex mineral phases with heavy metals that are found in relatively low

concentrations in the residues have also been suggested, e.g.  $\text{Cd}_5(\text{AsO}_4)_3\text{Cl}$  and  $\text{B}_3\text{Ti}_2\text{O}_2\text{F}_{10}$  (Eighmy et al., 1995). In general, such minerals should be considered carefully as they may indicate correlations of various elements in the solid rather than actual "identifications" of specific mineral phases.

## 2.4 Acid neutralizing capacity (ANC)

### *Determination of residue ANC*

The ability of the residues to neutralize acid, and thereby maintain a certain pH-level, can be characterized by the acid neutralizing capacity (ANC). The ANC is determined by titrating a residue suspension to a specific pH, typically pH 7.5 or 4.5 corresponding to determinations of the  $\rho$ -alkalinity and alkalinity with respect to the  $\text{H}_2\text{CO}_3^*$  equivalence point in an aqueous carbonate systems, see Box 2.2. Depending on the end-point-pH, the obtained ANC value reflects different portions of the entire buffer capacity. The buffer capacity of incineration residues may be associated to a large number of mineral phases, e.g. hydroxides, carbonates and silicates; Ca-minerals are generally considered most important in residue systems (Johnson, 1995).

ANC determined with respect to pH 7.5,  $\text{ANC}_{7.5}$ , is typically related to metal hydroxides and carbonates, whereas ANC determined with respect to pH 4.5,  $\text{ANC}_{4.5}$ , may include other minerals like silicates (Johnson, 1995; Johnson et al., 1999; IAWG, 1997). Typical values of  $\text{ANC}_{4.5}$  for APC residues are 6-10 meq/g (Polletini et al., 2001; IAWG, 1997). Astrup et al. (II) determined  $\text{ANC}_{4.5}$ , i.e. solid alkalinity, by measuring the remaining alkalinity in residue samples that had previously been equilibrated to specific pH-values, see Figure 1. The alkalinity data obtained here were in the range of 4-10 meq/g.

### *ANC depletion mechanisms*

The acid neutralizing capacity determined by titration reflects the material characteristics of a residue sample and may only be related to the neutralization behavior of the residue. In a real-life leaching scenario, acidity may be introduced to the residues from acidic rainwater infiltrating the disposal site, or from intrinsic acid producing reactions occurring in the residue matrix itself, e.g. degradation of organic compounds.

No reports have been found regarding characterization of organic matter degradation in APC residues, however, Ferrari et al. (2002) found that total organic carbon (TOC) in fly ashes was dominated by elemental carbon. In bottom ashes, degradation of organic matter has been found to be unimportant for buffer capacity depletion (Johnson and Furrer, 2002). Organic carbon in bottom ashes can be expected to be more degradable than organic carbon in APC residues (Ferrari et al., 2002). This indicates that the potential degradability of organic compounds in APC residues is low, and suggests that the potential depletion of ANC from acid producing reaction is low in these residues.

Astrup et al. (II) investigated the washout of solid alkalinity, or ANC, from various types of APC residues. It was found that leaching of alkalinity was highly

**Box 2.2.** Acid neutralizing capacity and alkalinity concepts with respect to APC residues (Johnson and Sigg, 1985; Stumm and Morgan, 1996; Johnson et al., 1995; Astrup et al., II).

Alkalinity in solid residues is typically referred to as acid neutralizing capacity (ANC). With respect to incineration residues, bottom ashes are the most investigated. Due to high contents of Ca in the residues, minerals like portlandite ( $\text{Ca}(\text{OH})_2$ ), calcite ( $\text{CaCO}_3$ ) and other basic Ca minerals such as ettringite ( $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ ) are most often associated with the buffer capacity (Johnson et al., 1995; Meima and Comans, 1997; IAWG, 1997). Alkalinity in incineration residues is measured analogous to aqueous solution by titrations, and is usually interpreted according to the carbonate system, see Stumm and Morgan (1996) for detailed description. Thus, alkalinity refers to the proton condition with respect to the equivalent solution of  $\text{H}_2\text{CO}_3^*$  and  $\text{H}_2\text{O}$ :

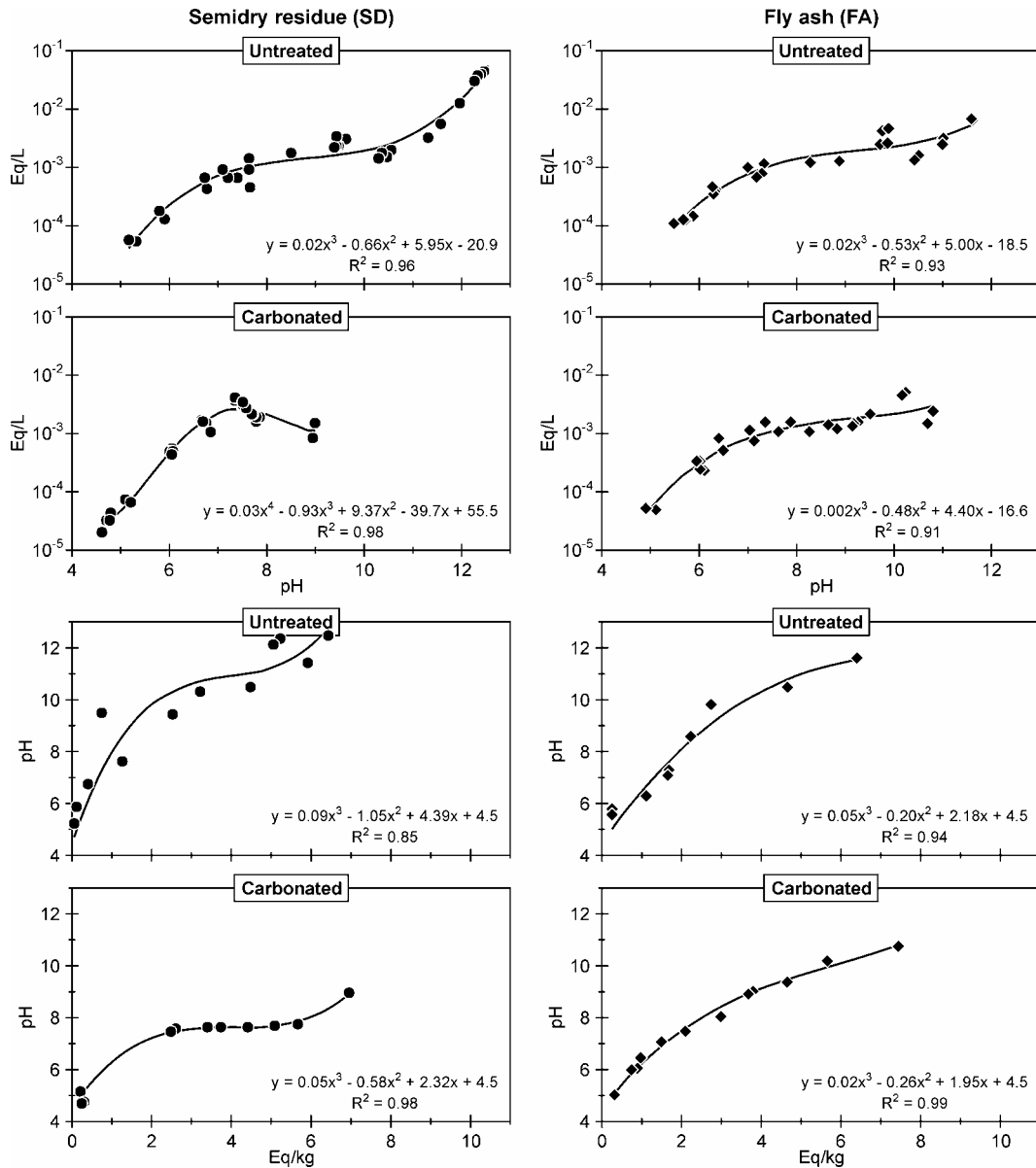
$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

However, also species like  $\text{Al}(\text{OH})_4^-$  and  $\text{H}_3\text{SiO}_4^-$  can be important (Johnson et al., 1999). An indication of the relative importance of Ca, Al or Si minerals for pH buffering may be assessed by measuring solution concentrations of these elements at specific pH-values during titration (e.g. Johnson et al., 1995). In the case of bottom ashes, it appears that Ca minerals are mainly responsible for the buffer capacity (Johnson et al., 1995).

To reflect the fact that removal of solid alkalinity in a residue leaching system is related mainly to leaching rather than neutralization, alkalinity may be categorized either as *leachable* or *residual* with respect to a specific pH (Astrup et al., II). Leachable alkalinity is the alkalinity that can dissolve from the solid matrix at a given pH, whereas the residual alkalinity is the remaining solid alkalinity at the same pH.

With respect to residue weathering, uptake of  $\text{CO}_2$  (carbonation) is very important. Assuming that alkalinity at high pH consists of hydroxides, e.g. portlandite and brucite ( $\text{Mg}(\text{OH})_2$ ),  $\text{CO}_2$  uptake may result in conversion of hydroxides into carbonates, e.g. calcite and magnesite ( $\text{MgCO}_3$ ). As the carbonates have a different solubility, the buffer characteristics of the residue have changed due to carbonation. It should be noted, however, that the total alkalinity of the residue does not change due to carbonation.

dependent on pH, see examples in Figure 1. Above pH 11, an almost linear relationship between alkalinity leaching and pH was observed and related to the  $\text{OH}^-$  concentration in the solution samples. In the pH range of 7-11 the leaching was more or less constant about  $10^{-3}$  eq/l, again linearly decreasing to about  $10^{-5}$ - $10^{-4}$  eq/l at pH-values below neutral. It was found that this behavior was qualitatively the same regardless of the pretreatment of the residue sample. This



**Figure 1.** Top half illustrates alkalinity leaching as a function of pH in individual batches for untreated (non-carbonated) and carbonated versions of semi-dry (SD) APC residue and fly ash (FA). Lower half illustrates pH in individual batches as a function of the solid alkalinity or ANC of the residues. Data are from Astrup et al. (II).

leaching of alkalinity, illustrated in Figure 1, was determined based on water extractions from residue samples previously equilibrated to specific pH-values (Astrup et al. II). No effects of acid neutralization was involved, hence the alkalinity released from the solid phase into the solution only reflects the depletion related to mineral dissolution. In actual leaching systems, this alkalinity may be transported by water percolating through the disposed residues and removed by leaching.

The ANC may also be depleted by neutralization with acidity contained in the infiltrating rainwater. Typical rainwater with a pH of 4.3 contains about  $5 \cdot 10^{-5}$

eq/l of acidity (Johnson & Sigg, 1985), which is about 2-5 orders of magnitude less than the alkalinity released to solution at pH-values above 7 (Astrup et al. **II**). This illustrates that depletion of ANC by neutralization with acidic rainwater is not important with respect to APC residues. Astrup et al. (**II**) concluded that the only important depletion mechanism was leaching.

#### *Developments in residue pH*

A major drawback of the ANC measure is that the changes in pH observed during titration cannot be related to actual leaching scenarios, unless the acid equivalents added are related directly to the acidity of rainwater. However, as rainwater only marginally affects depletion of ANC from the solid phase, this approach is not suitable for determining potential changes in pH due to progressive leaching at a disposal site.

Astrup et al. (**II**) related alkalinity leaching at specified pH-values (cf. Figure 1) to losses in solid alkalinity, or ANC, using a mass balance approach. This way it was possible to associate ANC depleted by leaching to the volume of water involved in this depletion. By relating the amounts of solid alkalinity remaining in the system to the residue pH that this alkalinity amount is associated with, a relationship between pH and L/S was established as shown in Figure 2. Although, variations in pH developments as a function of pH can be observed for the various APC residues in Figure 2, it is clearly seen that very high L/S ratios are required to lower pH to the acidic range (Astrup et al. **II**). For example, in order to reach pH 7 leaching at L/S ratios of about 2000-3000 l/kg is needed.

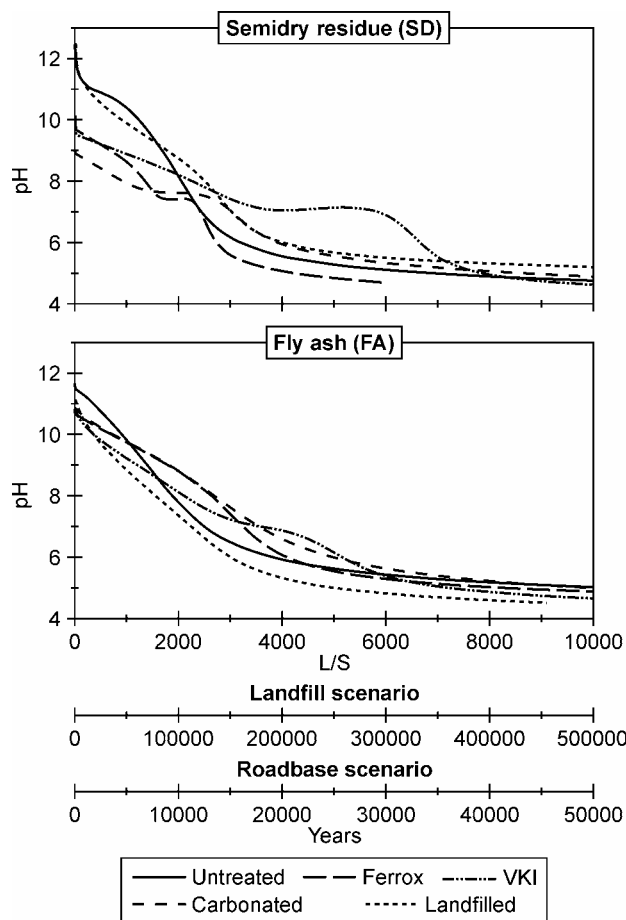
#### *Effects from carbonation*

Weathering of incineration residues involves dissolution of mineral phases and precipitation of new phases. In this context, uptake of atmospheric CO<sub>2</sub> and transformation of hydroxides into carbonates, i.e. carbonation, is especially important as this changes the buffer capacity of the residues, see Box 2.2 (Johnson et al., 1995; Meima and Comans, 1997). Astrup et al. (**II**) also investigated the potential effects on pH developments from carbonation. Although pH was initially lower, similar high L/S ratios were required to reach acidic pH-values as for the non-carbonated residues, see Figure 2. It should be noted that although the leaching needed to reach acidic pH-levels from an overall point of view was the same, the characteristics of the buffer capacity changed due to carbonation. This was most significant for the SD residue, where the buffer capacity significantly increased at pH 7-8 due to carbonation. This also resulted in a change in the shape of the pH-development curve for the SD residue after carbonation (Astrup et al. **II**).

## 2.5 Potential environmental impacts

The main environmental concerns regarding landfilling of APC residues are dust and gas emissions as well as leachate generation (Sabbas et al., 2003). Of these, leaching is by far the most important. Many of the metals listed in Table 1 may potentially leach in substantial amounts (e.g. Hjelm, 1996; IAWG, 1997, Sabbas





**Figure 2.** Leaching system pH estimated as a function of L/S (l/kg). Also included are time scales for a landfill (10 m high) and a roadbase (0.5 m high) leaching scenario. The residue density is assumed to 1 ton/m<sup>3</sup>, and the net infiltration rate to 200 mm/year. Data are from Astrup et al. (II).

et al., 2003). The ability of these residues to maintain high pH levels is very important in this respect as the leaching of most elements is affected by pH. For example, many cationic heavy metals, e.g. Cd, Pb and Zn, show increasing leaching when pH is decreasing in the acidic range (IAWG, 1997). Thus, it is commonly anticipated that leaching from APC residues may lead to elevated concentrations as the residue buffer capacity is depleted and pH decreases. However, due to the ability of these residues to maintain high pH-levels, such elevated metal concentrations may potentially require leaching for extremely long time (Astrup et al. II).

In order to properly assess the potential environmental impacts of APC residue disposal, it is necessary to evaluate the long-term leaching at solution conditions likely to occur in actual leaching systems. This involves accounting for the development in residue pH as leaching progresses. The following chapters will further discuss approaches for assessing this potential long-term leaching.

## 3. Leaching Characterization

### 3.1 Introduction

Leaching from incineration residues are characterized on the basis of a range of leaching tests: lysimeter, column and batch leaching test, see Box 3.1 for details. The most widely used tests are the batch leaching tests; especially the pH dependence test is used extensively for leaching characterization purposes (van der Sloot, 1990; van der Sloot et al., 1996; IAWG, 1997; Kosson et al., 2002). The pH dependence test provides information about the leaching as a function of pH usually at an L/S ratio of 10 l/kg (CEN, 2004).

Geochemical speciation modeling of pH dependent leaching data can provide information on possible solid phases that may control element concentrations in the leaching test solutions, i.e. determination of possible leaching control, see Box 3.2. Geochemical modeling and information about leaching control are prerequisites for predicting leaching beyond what can be assessed by experiments. However, if experimental data cannot reasonably well be explained with respect to leaching control by geochemical modeling, using such experimental data to evaluate or predict leaching in a long-term perspective may not be viable. The focus of geochemical modeling should be clear with respect to the interpretation of the modeling results. Geochemical modeling provides information pertaining to the specific conditions of the leaching test system from where the data are obtained, and the applicability of these conditions to real-life leaching systems should be kept in mind when evaluating the modeling results.

Only in a few cases has geochemical speciation modeling been used to evaluate leaching control in APC residues (Eighmy et al., 1995; van Herck et al., 2000; Gardner et al., 2002). None of these studies accounted for the high buffer capacities of APC residues and the potentially high L/S ratios needed to reach neutral or acidic pH-values.

This chapter focuses on characterizing the leaching from APC residues in a long-term perspective. Additionally, the possible implications of this characterization are discussed with respect to leaching tests.

**Box 3.1.** *Overview of important leaching test for granular residues (van der Sloot, 1990; van der Sloot, 2002; van der Sloot et al., 2001; Kosson et al., 2002; IAWG, 1997).*

Leaching tests are commonly arranged according to the complexity of the tests and the level of detail provided by the test. Basic characterization of residues involves lysimeter, column, pH dependence and availability testing, whereas more simple compliance testing includes batch leaching tests. Regulatory limit values are often related to batch tests.

**Lysimeter experiment.** A large-scale leaching experiment often involving several tons of residues. Typically, the residues are placed outside in an open container while allowing rainwater to infiltrate through the residues, and the generated leachate to be collected at the bottom of the container. As the natural infiltration rate determines the L/S ratio, years are often required to reach L/S 1.

**Column experiment.** A small-scale version of a lysimeter performed in the lab. Typically about 1-2.5 kg of residue is used in column tests. Infiltration is usually accomplished using a pump in an up-flow manner in order to minimize channeling and preferential flow. Depending on the flow rate, L/S 2 can be reached within a week, and L/S 10 in about a month. (CEN, 2003)

**pH-dependence test.** A batch leaching test at a fixed L/S ratio, usually L/S 10. Batches are set up with different pH usually covering the range of pH 4-12. pH is either maintained at a fixed level by continuous additions of acid to the residue suspension, or predetermined amounts of acid are added to the batches initially. In both cases, the reaction time is usually 48 hours. Equilibrium conditions are assumed to govern release to the test solution. The test aims to determine effects on leaching from changes in pH of the leaching system. (CEN, 2004)

**Availability test.** A two-step batch leaching test, each step usually at L/S 100. In the two leaching steps, pH is fixed at 7 and 4 for a specified time (often 6 and 18 hours, respectively) by continuous pH measurement and additions of acid. The test aims to determine the potential leachability of a residue by leaching at high L/S and low pH. (Nordtest, 1995; Fällman, 1997; NNI, 1994)

**Batch leaching test.** A one or two-step leaching test at L/S 10 or L/S 2 + 8. Leaching is performed at the natural pH of the residues, i.e. about pH 11-12.5 for APC residues, with an equilibration time of 24 hours. The tests are intended as a simple method for leaching testing relative to the above more detailed and complicated tests. (CEN, 2002). It should be noted that batch leaching tests provide data of the average leaching within the L/S ratio used in the test. This means that solution concentrations in an L/S 10 batch test are lower than the concentrations observed in a column test at L/S 2, and higher than the concentrations observed at L/S 10. However, the mass leached out in the batch test should resemble the mass leached out from the column at L/S 10. The "natural" pH of a residue is often assumed to resemble the pH observed in a batch test at L/S 2 or 10. Batch leaching tests may be performed in series in order to approximate progressive leaching.

**Box 3.2.** *Short introduction to leaching control and geochemical speciation modeling (e.g. van der Sloot, 1990; Kosson et al., 1996; IAWG, 1997).*

In batch leaching experiments, the leaching from granular residues may be interpreted with respect to solubility control or availability control. Solubility control indicates that specific minerals control solution concentrations according to specific solubility products. In this case, the solution concentrations essentially remain the same although the L/S ratio is varied. Availability control indicates that solution concentrations are below saturation with mineral phases and that all available mass of a given element is dissolved. In this case, the resulting concentrations will change due to variations in the L/S ratio. Interpretation of batch leaching experiments usually assumes that equilibrium conditions prevail in the leaching system. Leaching control with respect to mineral solubility or availability is most important, however other control mechanisms like sorption, incorporation into other phases, or redox reactions may also be considered.

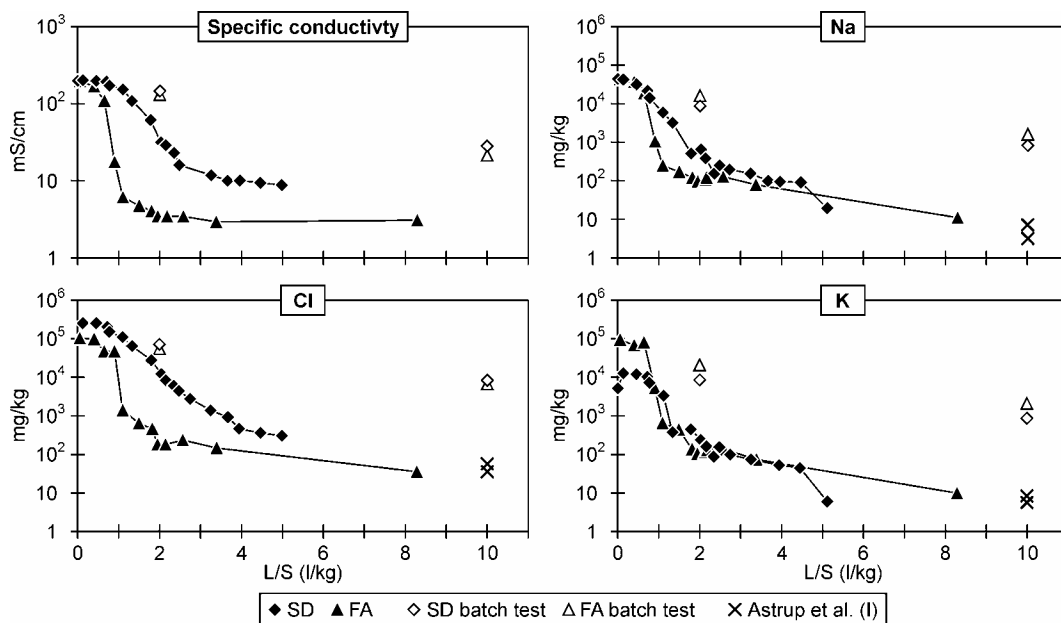
Geochemical modeling can be used to evaluate leaching control. Based on measured solution concentrations, geochemical models can calculate the activities of aqueous species while accounting for complexing agents, pH, Eh, ion strength, etc. Distribution of elements among solid phases may be included if desired. Saturation indices ( $SI = \log(I/AK/K_s)$ ) are calculated based on the solution speciation, and can be used to assess whether specific elements are close to saturation with mineral phases. Sorption may be considered by including specific surfaces for ion exchange or surface complexation, however this generally requires detailed information about the residue which is not the case for assessing solubility control.

It is important to realize that only aqueous species and solid phases containing the elements given as input to the geochemical model can be evaluated. Likewise, only the entities defined in the thermodynamic database can be included in the modeling. Therefore, it is important to include all

## 3.2 Short and long-term leaching

### *Leaching environment*

No rigorous definition of short and long-term leaching has been made, although many suggestions have been reported (e.g. Sabbas et al., 2003). For example, with respect to a specific disposal site it is natural to define the short term as the period of active operation and aftercare measures. Temporal aspects of leaching may also be related to the expected reactivity of the residues or to specific weathering reactions (Sabbas et al., 2003). However, definitions based on specific periods do not account for variations in material properties among residues. Definitions related to specific processes that occur in APC residue leaching systems, e.g. carbonation, may be very difficult to relate to time and are not practical for describing leaching in general. Here, it is proposed that short and long-term



**Figure 3.** Column leaching data for semi-dry (SD) residue and fly ash (FA) (data from Lundtorp, 2001). Data from batch leaching tests at L/S 2 l/kg and L/S 10 l/kg are shown for comparison (Jensen and Christensen, 1999). Data from leaching experiments with prior washing of the residues are also plotted at L/S 10 l/kg to illustrate the difference in salt load (data from Astrup et al., I).

leaching is related to the leaching environment, specifically with respect to the solution conditions of the leaching system.

Leaching from APC residues are characterized by very high salt concentrations in the initial leachate, however, these concentrations typically decrease several orders of magnitude within L/S 0-2 l/kg as illustrated in Figure 3. Thus, leaching at L/S ratios below 2 l/kg is characterized by salt concentrations significantly higher than leaching at higher L/S ratios. Although the exact L/S ratio when the salt concentrations approach a more constant value may vary according to the individual residue samples, L/S ratios of about 1-3 l/kg seem to be typical values. These observations are well established for incineration residues by studies involving column experiments, lysimeters and actual landfills (Hjelmar, 1996; Lundtorp, 2001; van der Sloot et al., 2001, IAWG, 1997). Leaching characterization is often performed using batch tests at L/S 2 or 10 l/kg, see Box 3.1. This implies that the high salt levels released in the initial leachate are included in the test solution of one-step batch tests at L/S 2 or 10 l/kg. A two-step batch leaching test, e.g. at L/S 2 and L/S 8 l/kg to obtain an accumulated L/S ratio of 10 l/kg, may remove a part of the salts in the first step, however, the solution concentrations at L/S 10 l/kg do not necessarily reflect those obtained from the column experiments. In the experiments shown in Figure 3, the salt concentrations in the first step of the batch test (L/S 2 l/kg) reasonably well reflect the column data, whereas the salt concentrations in the second step (L/S 10 l/kg) are significantly higher than the column data. This suggests that batch leaching

**Box 3.3.** *Relation between the liquid-to-solid (L/S) ratio and time (Hjelmar, 1990).*

The L/S ratio of an experimental leaching system, e.g. a column test or a batch test, may be related directly to a real-life leaching system such as a disposal site assuming homogeneous flow. The volume of water that comes into contact with the residues in a disposal site is determined by the infiltration rate at the site. Thus, time and L/S are related to the infiltration rate:

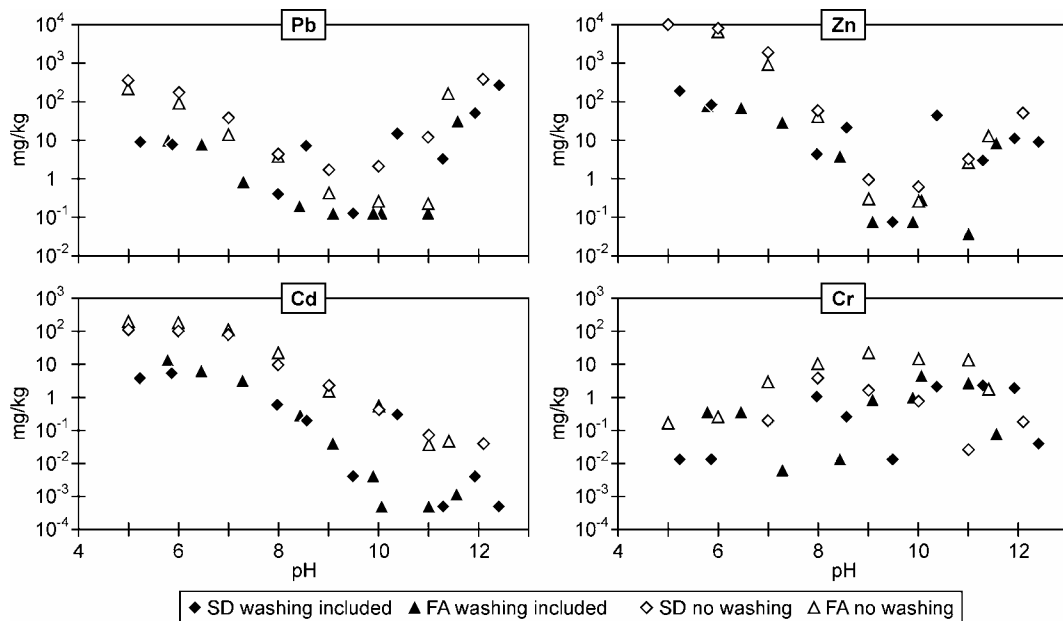
$$t = L/S \cdot \rho \cdot H/I$$

where  $t$  is the time after the first leachate appears at the bottom of the residue body (years),  $\rho$  is the dry bulk density of the residue,  $H$  is the height of the disposal site (m), and  $I$  is the net infiltration into the residues (m/year). For typical European landfills, the annual net infiltration may be assumed to be in the order of about 0.1-0.3 m/year. With a height of 10 m and assuming a residue bulk density of 1.3 kg/l, the leaching time may be close to 50 multiplied with the L/S ratio. Thus, it requires in average 50 years reaching an L/S ratio of 1 l/kg for such a disposal site. For an embankment with a height of 0.5 m and similar density and infiltration rate, the leaching time can be found

tests at L/S ratios of 2 l/kg and 10 l/kg represent leaching environments that are characterized by salt concentrations much higher than may be expected in real-life leachate.

As the concentration levels of Cl, K and Na appear to change dramatically in the course of a few L/S, the solution concentrations of other elements are likely to be affected due to changes in the leaching environment, i.e. effects from complexation and changes in ion strength. Generally, reasonable agreement has been observed for heavy metal leaching from bottom ashes between column leaching data and data from pH dependence tests at high pH-values (van der Sloot et al., 2001). Typical column leaching data have high pH close to the natural pH of the residues, e.g. pH 11-13 for APC residues, therefore such comparisons have been made only with pH dependent leaching data at these high pH-values. However, this agreement indicates that batch tests at L/S 10 l/kg can provide a reasonable estimation of the leaching at L/S 10 l/kg, provided the pH is similar to that of an actual leaching system at this L/S. On the other hand, significant differences were observed between the salt leaching at L/S 10 l/kg in the batch test compared with the column experiment in Figure 3. As the differences in ion strength between the test conditions in a batch leaching test and actual leachate concentrations are likely to increase with increasing L/S ratios, this suggests that leaching characterization based on batch tests should be carefully considered with respect to L/S ratios higher than 10 l/kg.

It should be realized that L/S ratios in the range of 0-10 l/kg does not necessarily imply short time in an actual leaching scenario, see Box 3.3. For example, a disposal site with a height of 10 m and a typical European infiltration



**Figure 4.** Data from pH dependence leaching tests on semi-dry (SD) residue and fly ash (FA) in the case of experiments including washing of the residues before leaching characterization (data from Astrup et al., **I**), and in the case of experiments with no washing included (Jensen and Christensen, 1999).

rate of 0.2 m/year will require about 50 years to reach an L/S ratio of 1 l/kg. Thus, the L/S ratio of 10 l/kg as used in the pH dependence test, see Box 3.1, corresponds to about 500 years for a typical disposal site.

#### Concentration levels

The effect of the salt load on leached concentrations of other elements may be evaluated by comparing pH dependent leaching data from experiments with and without prior removal of salts. Astrup et al. (**I**) investigated the pH dependent leaching after washout of the highly soluble salts. Residue samples were first equilibrated to specific pH-values, then washed and subsequently characterized with respect to leaching. The extra steps included here corresponded to an L/S ratio of about 33 l/kg in addition to the L/S 10 l/kg used in the test without washing. The specific conductivity in these experiments at the natural pH of the residues (pH 11.6-12.5) was about 5-10 mS/cm, which corresponds to the level for L/S ratios above 1-4 l/kg as observed in Figure 3. Concentrations of Cl, K and Na at the same pH are also shown in Figure 3, and although these data represent an accumulated L/S ratio higher than L/S 10 l/kg, the data match the column data rather well. This suggests that the data obtained by Astrup et al. (**I**) reflect the leaching conditions of actual leaching systems better than batch tests without washing.

In Figure 4, solution concentrations of Cd, Cr, Pb and Zn obtained by Astrup et al. (**I**) are compared with solution concentrations from a pH dependence test on the same residue samples without washing. In general, the presence of high

salt concentrations appears to cause metal concentrations about one order of magnitude higher than in the case with low salt concentrations. This suggests that the presence of complexing ligands and the higher ion strength significantly increases the metal concentrations. Complexation of heavy metals with inorganic ligands in natural systems has been demonstrated by numerous studies and the effect of ion strength on activity coefficients is well known (Stumm and Morgan, 1996). This effect may be evaluated at the natural pH of the residues because this pH reflects the pH-level of APC residue systems at low L/S ratios (cf. Figure 2). At this pH, Pb and Zn are present primarily as hydroxy complexes, whereas Cd is found mainly as Cl containing species, and Cr is present as  $\text{CrO}_4^{2-}$  (e.g. van der Sloot et al., 1996; van der Sloot et al., 2001).

At the natural high pH of the residues, the ion strength in the experiments without washing shown in Figure 3 and 4 has been found to 1.7-2.8 (L/S 2 l/kg) and 0.2-0.4 (L/S 10 l/kg) using PHREEQC (Parkhurst and Appelo, 1999). In the pH dependence test with washing, the ion strength was found to be 0.01-0.06 at the natural pH of the residues. In the column experiments discussed above, the ion strength was found to about 0.04 at L/S 4-5 l/kg. A difference in ion strength of about one order of magnitude between the pH dependent data at L/S 10 l/kg without washing and the column data may result in significant differences in activity coefficients. Using the Davies equation, the activity coefficient for divalent ions equals 0.5 and 0.3 in the two cases. Lower activity coefficients may result in higher solution concentrations in order to fulfill mass action laws.

### *Leaching test conditions*

As discussed above, the leaching environment may have a dramatic effect on the concentration levels of many elements in the leaching test solution. Hence, it is necessary to consider whether the solution conditions in a leaching test apply to the leaching scenario being evaluated. With respect to actual leaching systems, characterization of the leaching likely to occur above L/S about 2 l/kg should not include the highly soluble salts.

It has previously been explained that high L/S ratios are required to significantly decrease pH in leaching systems with APC residues (Astrup et al. II). The highly soluble salts like Cl, K and Na are therefore primarily leached at high pH-values. L/S ratios like 2-10 l/kg generally correspond to pH-levels close to the natural pH of the residues. High levels of salts are therefore not likely to be present in actual leaching systems at pH-values significantly below the natural pH. Accordingly, the solution conditions in the pH dependence test (L/S 10 l/kg) at pH levels below the natural pH may not reflect the conditions likely to occur in an actual leaching system, neither with respect to complexation nor ion strength.

This aspect should be related to leaching control as determined by geochemical speciation modeling. Such modeling is often done using data from pH dependence leaching tests (e.g. Eighmy et al., 1995; Ludwig et al., 2000; Meima and Comans, 1997). If the objective of the geochemical modeling is to determine the potential mechanisms controlling leaching at specific pH-values in actual leaching systems, then modeling pH dependent leaching without removing



the soluble salts may not be relevant at pH levels below the natural pH of the residue. Thus, geochemical modeling of leaching control in a long-term perspective, e.g. above L/S 10 l/kg, is likely more appropriate after washout of salts.

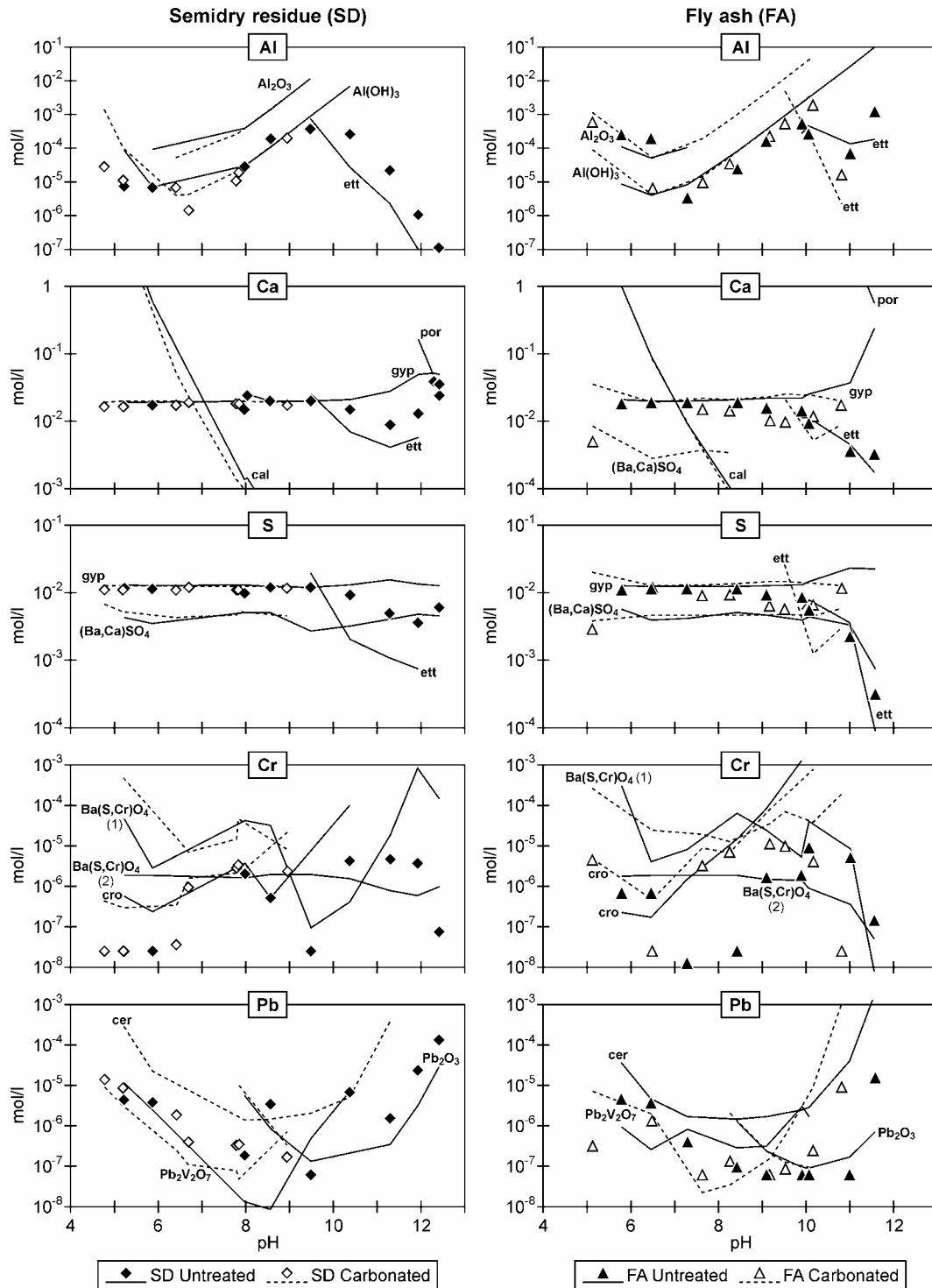
It is proposed that short-term leaching may be associated with the leaching occurring at solution conditions including the highly soluble salts, i.e. at L/S ratios below 2 l/kg in a column experiment and L/S 2-10 l/kg in a batch test. Consequently, long-term leaching is related to L/S ratios above 2 and 10 l/kg depending on the experimental context.

### 3.3 Leaching control

#### *pH dependent leaching*

In general, the leaching of Cl, K and Na is controlled by the availability for leaching rather than mineral solubility (IAWG, 1997). Eighmy et al. (1995) investigated leaching control as a function of pH and found that major elements such as Al, Ca, Mg and S were controlled by solubility of the minerals  $\text{Al}(\text{OH})_3$ , anhydrite ( $\text{CaSO}_4$ ) and magnesite ( $\text{Mg}(\text{CO}_3)$ ). The heavy metals Cd, Cr, Cu, Pb and Zn, which may all be leached in high concentrations from APC residues, were found to be controlled by otavite ( $\text{CdCO}_3$ ), crocoite ( $\text{PbCrO}_4$ ),  $\text{Cu}(\text{OH})_2$ , anglesite ( $\text{PbSO}_4$ ), cerrusite ( $\text{PbCO}_3$ ),  $\text{ZnSiO}_3$  and smithsonite ( $\text{ZnCO}_3$ ).

Astrup et al. (I) investigated the pH dependent leaching after washout of salts and found that the leaching of Al, Ba, Ca, Cd, Cr, Pb, S, Si, V and Zn was generally controlled by mineral solubility in the range of pH 4.5-12.5, see examples in Figure 5. Table 3 lists the minerals found likely for solubility control by Astrup et al. (I), as well as controlling minerals found by other studies. In the experiments performed by Astrup et al. (I), solution concentrations of Al, Ca and S appeared to be controlled by ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ) above pH 9.5-10. Below this pH, Al solubility was controlled by amorphous  $\text{Al}(\text{OH})_3$ , whereas Ca and S was controlled by anhydrite. Ba was close to saturation with barite ( $\text{BaSO}_4$ ) and a solid solution with Cr ( $\text{Ba}(\text{S,Cr})\text{O}_4$ ). The solubility of this solid solution appeared to be close to saturation of S and Cr as well, although the Cr mole fraction of the solid solution affected how well the Cr data were predicted. Also, crocoite ( $\text{PbCrO}_4$ ) was reported to be a likely controlling mineral below pH 8-9. However, Cr was found to show somewhat varying solution concentrations as some data points were about two orders of magnitude lower than neighboring data points at similar pH (Astrup et al. I). Pb appeared to be controlled mainly by the solubility of  $\text{Pb}_2\text{V}_2\text{O}_7$  and  $\text{Pb}_2\text{O}_3$  and V by the solubility of  $\text{Pb}_2\text{V}_2\text{O}_7$  and  $\text{Pb}_3(\text{VO}_4)_2$ , although these minerals could not explain V leaching above pH 10-11. Possibly, V leaching could be affected by incorporation into other minerals. Willemite ( $\text{Zn}_2\text{SiO}_4$ ) was important for leaching of Zn. Cd was observed to be controlled primarily by otavite ( $\text{CdCO}_3$ ) and the solid solution  $\text{Ca}_4\text{Cd}(\text{PO}_4)_3\text{OH}$ . However, also other mechanisms like sorption were suggested



**Figure 5.** Measured solution concentrations of Al, Ca, S, Cr and Pb as a function of pH for untreated (non-carbonated) and carbonated versions of semi-dry (SD) residue and fly ash (FA). Solid and dashed lines represent model predicted equilibrium concentrations for the untreated and carbonated residues, respectively. Model predictions are shown only for saturation indices within  $\pm 3$ . If the model lines coincided, only the solid lines for non-carbonated residues are shown. Abbreviations are: anh: anhydrite,  $\text{Ba}(\text{S,Cr})\text{O}_4(1)$ :  $X_{\text{Cr}} = 0.23$ ; (2):  $X_{\text{Cr}} = 0.50$ ; (3):  $X_{\text{Cr}} = 8 \times 10^{-5}$ , cal: calcite, ett = ettringite, por: portlandite, cer: cerrusite, cro: crocoite. Data are from Astrup et al. (1).

**Table 3.** Overview of mineral phases suggested for solubility control in non-stabilized waste incineration APC residues.

Element	Astrup et al. (I)	Other investigations	References
Al	Al <sub>2</sub> O <sub>3</sub>	Al(OH) <sub>3</sub> AlOOH	b, c, d
	Al(OH) <sub>3</sub> (a)		
	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O		
Ba	Ba(S,Cr)O <sub>4</sub>		
	(Ba,Ca)SO <sub>4</sub>		
	BaSO <sub>4</sub>		
Ca	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaCO <sub>3</sub> CaSO <sub>4</sub> CaSO <sub>4</sub> ·2H <sub>2</sub> O	a, b, c
	Ca(OH) <sub>2</sub>		
	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O		
	(Ba,Ca)SO <sub>4</sub>		
Cd	CdCO <sub>3</sub>	CdCO <sub>3</sub> Ca(OH) <sub>2</sub>	c, d
	Ca <sub>4</sub> Cd(PO <sub>4</sub> ) <sub>3</sub> OH		
	CdSiO <sub>3</sub>		
Cr	Ba(S,Cr)O <sub>4</sub>	PbCrO <sub>4</sub>	c
	PbCrO <sub>4</sub>		
Pb	Pb <sub>2</sub> O <sub>3</sub>	Pb(OH) <sub>2</sub> PbSO <sub>4</sub> PbCO <sub>3</sub> Pb <sub>4</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	a, c, d
	Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub>		
	PbCO <sub>3</sub>		
S	CaSO <sub>4</sub> ·2H <sub>2</sub> O	CaSO <sub>4</sub>	c
	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O		
	(Ba,Ca)SO <sub>4</sub>		
Si	KAlSi <sub>2</sub> O <sub>6</sub>		
	CaAl <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> ·2H <sub>2</sub> O		
	CaSiO <sub>3</sub>		
V	Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub>		
	Pb <sub>3</sub> (VO <sub>4</sub> ) <sub>2</sub>		
Zn	Zn <sub>2</sub> SiO <sub>4</sub>	ZnSiO <sub>3</sub> ZnCO <sub>3</sub> Zn(OH) <sub>2</sub>	a, c, d
	ZnO		
	CaZn <sub>2</sub> (OH) <sub>6</sub> ·2H <sub>2</sub> O		
	ZnCO <sub>3</sub>		

a) Gardner (1991)

c) Eighmy et al. (1995)

b) Kirby and Rimstidt (1994)

d) van Herck et al. (2000)

to affect Cd leaching as Cd concentrations in part of the pH-range could not be explained by mineral solubility (Astrup et al. I).

Most of the controlling minerals identified by Eighmy et al. (1995) were also found by Astrup et al. (I), although the modeling done by Astrup et al. (I)

provided a significantly better prediction of the measured solution concentrations and identification of several new mineral phases likely for solubility control. The fact that most salts were washed out by Astrup et al. (I), before leaching characterization, may have improved the possibilities of modeling the experimental data. The fact that the model results of the two investigations show common minerals, indicate that the geochemical models are able to properly account for the different leaching environments, and that the minerals identified reflect actual properties of the residues.

Overall, the pH dependent leaching appears to be controlled primarily by mineral solubility, at least after washout of the salts. Sorption and redox processes were not included in the modeling, still these processes appear to be of only minor importance, except in the case of Cd and Cr. V may be affected by other mechanisms, e.g. incorporation into other minerals at high pH. Cr(VI) is highly toxic and very mobile in the environment (Rai et al., 1989; Richard and Bourg, 1991), consequently Cr may be one of the most important elements in APC residue leachate not entirely controlled by mineral solubility.

#### *Effects from carbonation*

Carbonation may result in formation of new minerals and thereby induce changes in solubility control. However, as illustrated in Figure 5, the solution concentrations do not appear to change significantly in the experiments where salts were removed (Astrup et al. I). Only Cd leaching from the semi-dry residue appeared to be significantly affected by carbonation. This resulted in solution concentrations about two orders of magnitude lower than in the case of non-carbonated samples. Generally, the same mineral phases were identified likely for solubility control of carbonated samples and non-carbonated samples.

Overall, this suggests that the mineral phases found to control leaching of the elements Al, Ba, Ca, Cd, Cr, Pb, S, Si, V and Zn may reflect actual leaching systems as the minerals appear to be important both before and after carbonation.



## 4. Leaching Prediction

### 4.1 Introduction

Characterization of leaching from APC residues with respect to potential environmental impacts must include a long-term perspective as discussed in the previous chapters. Leaching control may be evaluated by geochemical modeling of data from pH dependent leaching tests by accounting for the leaching environment likely to occur at an actual disposal site. However, leaching data or geochemical modeling of such data alone do not provide us with information about the actual leachate concentrations to be expected from a disposal site at L/S ratios above 10 l/kg, nor do we obtain information about the rates by which elements are depleted from the solid residues.

Potential long-term leachability of incineration residues is often determined based on availability tests (Fällman, 1997; Nordtest, 1995; Kosson et al., 2002), see Box 3.1. Often a high L/S ratio of 200 l/kg is used in conjunction with low pH to minimize the influence of solubility control, i.e. to allow solid phases to dissolve completely, if possible. The potential leachability as determined by the availability test is defined with respect to the specific solution conditions of this test rather than criteria related to actual leaching scenarios. This means that availability data may have limited value for predictive or assessment purposes as the data cannot be related to the L/S ratio of a leaching system (Astrup et al. III).

This chapter introduces a new approach for predicting long-term leaching based on experimental leaching data, and evaluates the long-term leaching from APC residues. Finally, the implications for leaching tests interpretation are discussed.

### 4.2 Relating L/S to actual leaching scenarios

The L/S ratio of a leaching experiment can be directly related to the L/S ratio of a real-life leaching system, such as a disposal site, and may readily be converted into time for a specific hydraulic regime as shown in Box 3.3. However, this is possible only for leaching data that reasonably well represent actual leaching, i.e. column or lysimeter leaching experiments. The pH of the leaching solution is a key parameter affecting leaching. Batch experiments at L/S 10 l/kg have been found to agree well with column experiments, as previously discussed, and may thus represent actual leaching adequately. Batch experiments at higher L/S ratios, however, may not reflect the solution conditions of actual leaching scenarios as the test solution becomes more diluted.

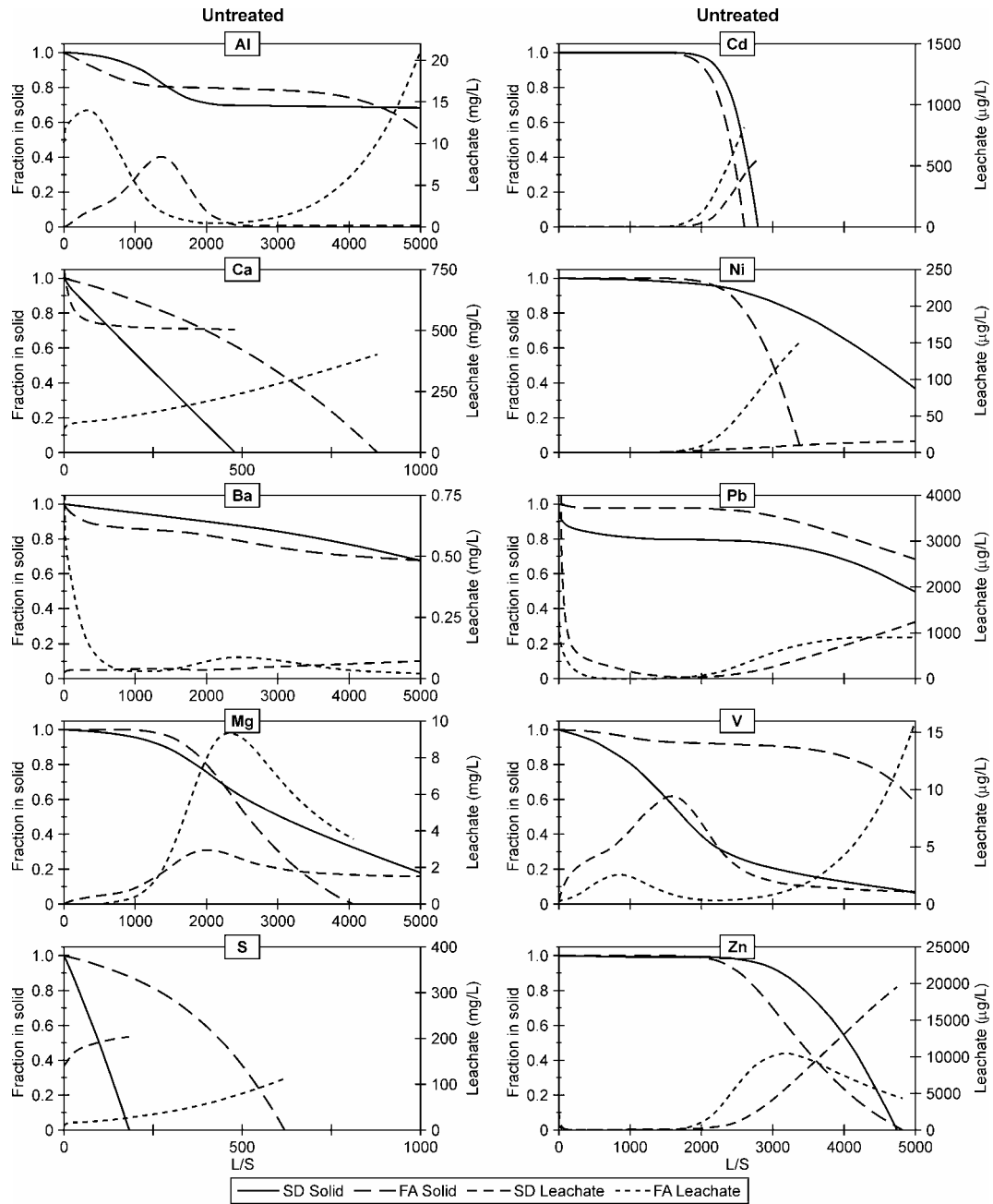
In order to characterize leaching, and specifically leachate concentrations, in a long-term perspective not covered by experimental leaching data, it is necessary to employ modeling. Astrup et al. (III) combined the pH dependent leaching data from Astrup et al. (I) with the long-term pH development estimated by Astrup et al. (II) to predict the leaching as it may occur in actual leaching systems. Specifically, the pH dependent leaching data was plotted as a function of the L/S ratio corresponding to the pH of the leaching data. Thus, a relation between the element concentrations and L/S of a leaching system was provided as shown in Figure 6. It should be realized that the shape of the resulting leaching curve is a combination of the characteristics of the pH development curve shown in Figure 2 and the pH dependent leaching as shown in Figure 5. Note that for practical reasons, the leaching curves have been determined based on polynomials approximated to the experimental data (Astrup et al. II, III).

This approach assumes that the leaching is characterized by equilibrium conditions and that the flow pattern in the leaching system is homogeneous. The first assumption was investigated by Astrup et al. (I), who found that the pH dependent leaching were generally controlled by equilibrium conditions as discussed in the previous chapter. The long-term leaching of Cr was not predicted as Cr appeared to be significantly affected by redox conditions in the leaching test. The contact time in these experiments was 24 hours. In real-life leaching systems, the residence time is likely to be significantly longer (Johnson et al., 1998; Ludwig et al., 2000). Thus, it is reasonable to assume local equilibrium conditions. The flow patterns in granular APC residues have not yet been investigated. Preferential flow has been reported for bottom ashes (Johnson et al., 1998), suggesting that preferential flow may also exist in APC residue disposal sites. However, considering the very long time frames involved in leaching from APC residues, it may be justifiable from an overall point of view, to assume homogeneous flow.

### 4.3 Long-term leachate concentrations

Astrup et al. (III) estimated long-term leachate concentrations in an L/S range of 0-5000 l/kg (cf. Figure 6). The concentration levels reported below, represent leaching after washout of soluble salts (Astrup et al. III). In Table 4, these concentrations are compared with data from a batch test at L/S 2 and 10 l/kg.

Astrup et al. (III) estimated the long-term concentrations of Ca and S to 100-750 mg Ca/l and 9-20 mg S/l (Figure 6). Ca concentrations appeared to decrease with increasing L/S ratio for the semi-dry (SD) residue, whereas the concentrations slightly increased for the fly ash (FA). The estimated Ba concentrations were low compared with Ca and S (typically 0.02-0.08 mg Ba/l after L/S 500 l/kg). The initial Ba concentrations for the SD residue, however, were found to be 1.1 mg Ba/l and to decrease rapidly within L/S 500 l/kg. Al concentrations increased to 8-14 mg Al/l at L/S 400 l/kg (FA) and L/S 1500 l/kg (SD), and thereafter concentrations decreased to about 0.5 mg Al/l. From L/S 3000 l/kg, leachate concentrations for the FA residue were estimated to increase



**Figure 6.** Estimated long-term leaching of major elements (as percentage remaining in the solid) and leachate concentrations (mg/l) as a function of L/S (l/kg), after the initial washout of highly soluble salts. The curves for leachate concentrations are truncated when an element is depleted from the solid phase. Please note that the initial Ba concentration was 1.1 mg/l for the FA residue, and that the initial Pb concentration was 31 mg/l for the SD residue. Data are from Astrup et al. (III).

to 20 mg Al/l at L/S 5000 l/kg. Mg concentrations were estimated to be less than 1 mg Mg/l at L/S ratios below 1000 l/kg. Afterwards, the concentrations increased to a maximum after about L/S 2000-2400 l/kg with concentrations of 3-9 mg Mg/l.



**Table 4.** Leachate concentrations in batch leaching tests (L/S 2 and 10) (Jensen and Christensen, 1999) and estimated long-term leachate concentrations for semi-dry (SD) residue samples and fly ash (FA) samples (Astrup et al., III). Units are mg/l.

	Batch test (L/S 2)		Batch test (L/S 10)		Long-term prediction
	SD	FA	SD	FA	SD and FA
Al	0.8	0.2	0.3	0.1	0.5-20
Ca	28,000	3200	4100	1300	100-750
Ba	4	2	0.04	0.003	0.02-1
Mg	1	< 0.9	< 0.9	< 0.9	1-9
S	300	1100	400	700	9-20
Cd	14	0.03	0.004	0.005	0.01-0.9
Ni	0.3	0.07	0.03	0.03	0.001-0.2
Pb	290	1	40	20	0.1-30
V	-	-	-	-	0.005-0.02
Zn	17	3	5	1	0.05-20

Cd and Ni were both leached in very low concentrations below L/S 1500 l/kg, i.e. less than 10 µg Cd/l and 1 µg Ni/l. At higher L/S ratios, concentrations increased gradually to 600-900 µg Cd/l and 150 µg Ni/l. The amphoteric metals, Pb and Zn, behaved differently as they had high concentrations in the first part of the leaching (2-30 mg Pb/l and 0.6-3 mg Zn/l). However, after L/S 100 l/kg, the concentrations were below 1 mg Pb/l and 0.2 mg Zn/l. At L/S 1000-2000 l/kg, Pb concentrations had a minimum of about 0.1 mg Pb/l and were thereafter increasing to about 1 mg Pb/l. Zn concentrations were below 0.05 mg Zn/l until L/S 1500 l/kg, and then increased to 10-20 mg Zn/l at L/S 3000-5000 l/kg. The leachate concentrations of V were low compared with the other elements; less than 16 µg V/l was estimated to leach out. Below L/S 700 l/kg, the concentrations were less than 5 µg V/l.

For most elements, the long-term leachate concentrations remain close to the initial level or decrease as the leaching progresses. Generally, Astrup et al. (III) found it likely that the most elevated leachate concentrations within L/S 2000 l/kg, corresponding to about 100,000 years for a typical disposal site, are the concentrations associated with the initial leachate below L/S 10 l/kg. However, Al and Mg were predicted to have higher leachate concentrations within L/S 2000 l/kg than the concentrations observed in batch experiments at L/S 2 and 10 l/kg, see Table 4.

These observations are very important with respect to assessments of environmental impacts as the leachate concentration levels reflect the toxicity of the leachate. When evaluating potential impacts, it is important to know the temporal variations in the leachate concentrations in order to account for these,

**Table 5.** Element leaching measured at L/S 10 (values correspond to L/S 10 solution concentrations in Table 4; Jensen and Christensen, 1999) and estimated for L/S 500 (values in parenthesis include the leaching at L/S 10; Astrup et al., **III**). The leaching predicted by the availability test (Lundtorp, 2001) is listed for comparison together with the corresponding L/S ratios estimated from Figure 6.

	L/S 10 (%)		L/S 500 (%)				Availability (%)		"L/S" (l/kg)	
	SD	FA	SD		SD	FA	SD	FA	SD	FA
Al	0.0	0.0	2	(2)	10	(10)	8	15	1000	800
Ca	16	6	100	(100)	41	(47)	86	77	400	800
Ba	0.1	0.0	2	(2)	12	(12)	22	17	3800	1800
Mg	0.1	0.1	1	(1)	0.04	(0.1)	48	52	2900	2600
S	13	23	100	(100)	63	(86)	86	86	200	600
Cd	0.0	0.0	0.02	(0.2)	0.01	(0.01)	83	96	2700	2600
Ni	0.5	0.2	0.4	(0.9)	0.06	(0.3)	29	14	3800	2500
Pb	7	3	17	(24)	2	(5)	27	42	3600	>5000
V	-	-	7	-	1	-	-	-	-	-
Zn	0.2	0.1	0.4	(0.6)	0.2	(0.3)	67	68	4300	3800

i.e. impacts occurring within the first 100 years may be rated differently than impacts occurring after 100,000 years (e.g. Hellweg, 2000).

It can be noted that very high leachate concentrations of Cd, Pb and Zn due to low pH-levels may require extremely long time to occur. Very high concentrations of Pb and Zn are more likely to occur within the initial period of leaching at high pH. With respect to residue stabilization, this clearly suggests that focus should be placed on controlling the leaching at high pH rather than at low pH. In other words, characterizing leaching behavior as a function of pH may be relevant from a material characteristics point of view; however, focusing on the concentration levels in the acidic range may be of limited value with respect to real-life leaching scenarios.

#### 4.4 Solid phase depletion

Another approach to assess long-term leaching is to focus on the depletion of various elements from the residue matrix. This was done by Astrup et al. (**III**) using mass balance calculations for relating the predicted long-term leachate concentrations to decreases in solid content (Figure 6). As these long-term leachate concentrations have been based on experiments with the highly soluble salts being removed, solid phase depletion also necessitate consideration of the initial removal. Table 5 lists decreases in solid contents associated with short-term leaching, here defined by an L/S 10 batch test, as well as decreases associated with long-term leaching as represented by L/S 500 l/kg. Only the solid contents of

Ca, S and Pb were significantly affected by short-term leaching. The leaching discussed below includes this initial leaching (Astrup et al. **III**).

The main part of Al, Ca, Ba and S (about 20-100 %) leached at L/S ratios below 500-1000 l/kg, although the leachate concentrations were relatively high initially. Ca and S were completely depleted within the first 300-800 l/kg, although Ca and S were both present in the residues in high concentrations (about 200-250 g/kg and 30 g/kg, respectively). The main fraction of solid Mg was leached after L/S 1000 l/kg as the Mg concentrations were relatively low in the beginning and significantly increasing after L/S 1000 l/kg (80-100 % was leached at L/S 5000 l/kg). Al was leached primarily at high pH and at low pH, this caused the leaching to occur mainly below L/S 1000-2000 l/kg and then again at L/S ratios above 4000-5000 l/kg (30-50 % was leached at L/S 5000 l/kg).

The heavy metals Cd, Ni and Zn mainly leached at L/S ratios above 2000 l/kg. Pb concentrations in the leachate were initially very high resulting in substantial leaching below L/S 200 l/kg. After this, Pb concentrations were relatively low, however the concentrations increased again at L/S 3000 l/kg resulting in further removal from the solids (30-50 % was leached at L/S 5000 l/kg). Between 40 % (FA) and 90 % (SD) of solid V was estimated to leach out at L/S 5000 l/kg.

In general, Astrup et al. (**III**) found that long term leaching from the investigated APC residues was qualitatively similar in spite of the differences in ash composition and natural pH. Except for Ca, S and Pb, leaching in significant fractions of the solid concentrations was found to require very high L/S ratios typically above 1000-2000 l/kg, corresponding to about 50,000-100,000 years for a typical disposal site.

Table 5 lists the potential leaching in fractions of the total element content as estimated by the availability test. Also listed are the L/S ratios required to leach these fractions, based on the depletion rates discussed above. For all elements except Al, Ca and S, these L/S ratios were in the order of 1000-5000 l/kg, illustrating that the availability data can be related neither to the L/S ratio of the test nor to a specific higher L/S ratio. Further, as the availability data correspond to leaching for extremely long periods of time, these data may not be useful for assessment purposes.

#### 4.5 Effects of carbonation on long-term leaching

Although carbonation was found to affect the characteristics of the residue buffer capacity as previously discussed, the actual leaching as a function of pH was for most elements not significantly altered (Astrup et al. **I, II**). However, carbonation will likely affect the pH development by decreasing pH at a faster rate than observed for a non-carbonated residue, and thus approach the pH development curve for the carbonated residue samples in Figure 2. This effect on pH may be assessed by comparing the long-term leaching from the carbonated residue samples with the non-carbonated.

For all investigated elements except Al, Ca and S, the removal from the solid phase occurred at a similar or slower rate from the carbonated residues compared with the non-carbonated residues (Astrup et al. **III**). The leaching of Al from the carbonated SD residues was decreased compared with non-carbonated samples resulting in less removal from the solid phase, whereas the leaching from the carbonated FA residue was increased at lower L/S ratios leading to a faster removal. The leaching of Ca and S was observed to increase with decreasing pH in the range of pH 9-12 (cf. Figure 5). As pH of the carbonated samples initially was lower than pH of the non-carbonated samples, the low leaching of Ca and S, observed from the non-carbonated samples, is not included in the leaching curves for the carbonated residues. This results in a faster depletion from the carbonated samples as opposed to the non-carbonated samples.

Overall, the long-term leaching does not appear to increase significantly due to carbonation. Al, Ca and S were depleted faster: Ca and S about 50-500 l/kg earlier than without carbonation. Al was not depleted within L/S 5000 l/kg, regardless of level of carbonation.

#### 4.6 Implications for leaching characterization

The prediction of long-term leaching discussed in this chapter illustrates the importance of considering the leaching history, i.e. the concept of progressive leaching, when interpreting pH dependent leaching data. For example, Ca and S may be depleted at L/S ratios within 300-900 l/kg (Astrup et al., **III**). These L/S ratios correspond to pH-values about 10-11 for non-carbonated and pH 8-10 for carbonated residue samples (cf. Figure 2). This suggests that discussions concerning leachate concentrations and leaching control involving Ca and S at pH-values lower than these should consider the possibility of Ca and S being depleted. Accordingly, it may not be relevant to discuss Ca and S concentrations in a pH dependence test at low pH-values if the data are used for predictive purposes. Leaching control from Ca and S containing minerals may likewise not be relevant at low pH.

These considerations suggest that leaching control from anhydrite ( $\text{CaSO}_4$ ) may not be relevant at pH below 10, and that Ca and S may be depleted while solution concentrations are controlled by the relatively lower solubility of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ). Al leaching was also found to be controlled by ettringite, however at pH-values below 10  $\text{Al}(\text{OH})_3$  appears to be the controlling mineral. Assuming depletion of Ca and S at pH 10, Si leaching seems more likely to be controlled by leucite ( $\text{KAlSi}_2\text{O}_6$ ) than wairakite ( $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ ) below pH 10. Similarly, it may be argued that crocoite ( $\text{PbCrO}_4$ ) is more important for solubility control of Cr than a  $\text{Ba}(\text{S,Cr})\text{O}_4$  solid solution at these pH-values.

In the investigations by Astrup et al. (**III**), leaching prediction was based on local equilibrium conditions and homogeneous flow situations. As discussed above, leaching in real-life leaching systems may be affected by preferential flow. This suggests, depending on the specific hydrology of the disposal site, that

kinetics can play a role. In this case, depletion from the solid phase may occur at a slower rate as compared with situations with equilibrium and homogeneous flow. These issues should be addressed for APC residues and considered with respect to detailed geochemical modeling.

With respect to leaching prediction in more detail, geochemical modeling should be involved as a tool for predicting the leaching as a function of L/S. This requires that the relevant minerals are identified and that the governing mechanisms for leaching control are understood. This information should be included in the modeling approach. Presently, this has not been done, however the work presented by Astrup et al. (**I**, **II**, **III**) provides the basis for pursuing this path. The possible consequences for the predicted leaching from non-homogeneous flow situations and non-equilibrium should further be evaluated for APC residues.

Leaching of specific heavy metals like Cd, Cr and V may not be adequately predicted only by mineral solubility. The possible importance of other processes should be addressed further. In this context, it was found that Cr was an important element due to the high mobility and toxicity of Cr(VI) in the environment. The following chapter will focus on Cr leaching control in detail.

## 5. Cr Leaching

### 5.1 Introduction

In natural systems, Cr exists either as Cr(III) or Cr(VI) (Rai et al., 1989; Richard and Bourg, 1991). Cr(III) is relatively insoluble in the range of pH 6-12 while Cr(VI) typically has a very high solubility. As such, Cr(III) is rather immobile in most natural systems while Cr(IV) is very mobile. Most attempts to control Cr(VI) transport in the environment focus on redox transformation of Cr(VI) into Cr(III) (e.g. Eary and Rai, 1988; Astrup et al., 2000).

Cr in APC residues is generally considered to be present as Cr(VI). Although it has not yet been proven analytically, this is most likely the case considering the oxidized and high pH characteristics of APC residues. In incineration ashes, steel slag, and coal fly ashes Cr(VI) has been suggested to be controlled by solubility of Ba(S,Cr)O<sub>4</sub> solid solutions (Fruchter et al., 1990; Kersten et al., 1998; Fällman, 2000; Astrup et al. I). Cr leaching from waste incineration residues has often been observed to vary significantly and be inconsistent (Cai et al., 2003; Astrup et al. I), although Cr leaching in some cases also appeared to be more stable (Kersten et al., 1998). Cr concentrations in APC residue leachate are typically found in the range of a few µg/l to a few mg/l within pH 4-12 (Hjelmar, 1996; van der Sloot et al., 2001). Astrup et al. (I) concluded it likely that Cr leaching from APC residues was affected by mechanisms other than solubility control.

The apparent inconsistencies in Cr leaching behavior have been related to the redox conditions of the investigated residues. For example, low Cr leaching from bottom ashes compared with high Cr leaching from APC residues has been interpreted as Cr being present as Cr(III) in the bottom ashes and as Cr(VI) in the APC residues (van der Sloot, 2001). The importance of redox conditions in the leaching test system has also been pointed out (Fällman and Aurell, 1996; Cai et al., 2003; Chen et al., 2003). For example, high Cr leaching has been associated with the presence of O<sub>2</sub> in leaching test solutions, and has been interpreted as possible oxidation of Cr(III) (Ecke, 2003; Cai et al., 2003). With respect to chemical stabilization of residues, it has been found that the stabilization process itself enhance Cr leaching (Hjelmar et al., 2001; Lundtorp, 2001; Sørensen, 2001; Cai et al., 2003). Astrup et al. (I) observed that in the pH range of 4.5-12.5 some batch experiments resulted in Cr concentrations significantly lower than other batches with similar pH.

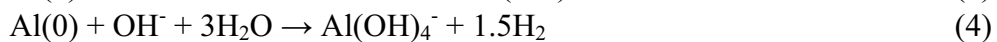
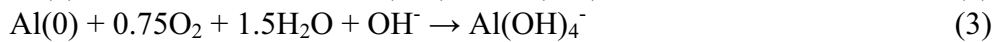
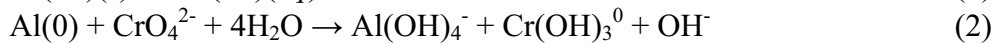
Leaching of Cr from APC residues appears to be highly affected by the conditions in the leaching test and especially influenced by the redox conditions. Consequently, Cr leaching may not be evaluated only by solubility control, and long-term Cr leaching may not be predicted entirely based on equilibrium conditions.

This chapter provides a coherent explanation of Cr leaching behavior with respect to leaching test conditions, and discusses the implications of leaching testing and residue treatment.

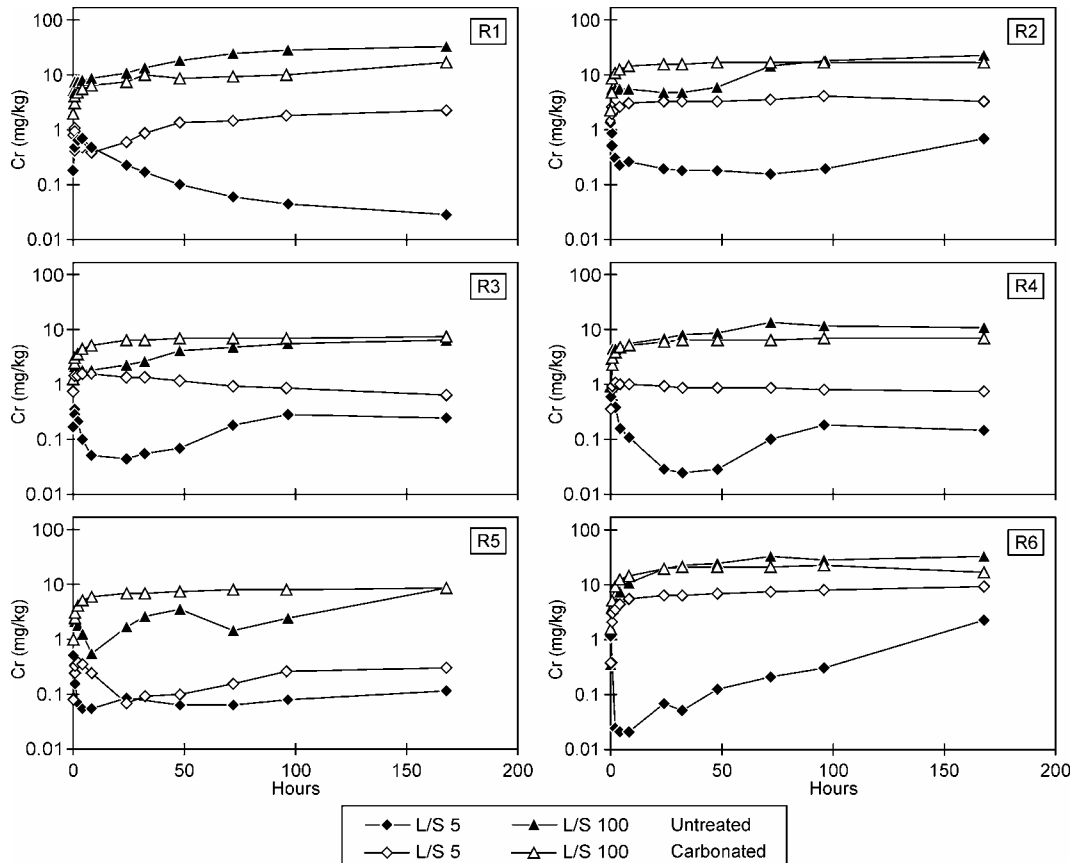
## 5.2 Al-O<sub>2</sub>-Cr interactions

A few studies have suggested that Al(0) may potentially reduce Cr(VI) in ash systems (Abbas et al., 2001; Cai et al., 2003), either related to intrinsic reactions occurring in ash systems or related to residue stabilization by Al(0) additions. Metallic aluminum has been identified in APC residues (Forestier and Libourel, 1998), and has been associated with H<sub>2</sub> generation in ashes (Lechner et al., 1997; Mizutani et al., 2000; Magel et al., 2001). Al(0) added to residue leachate has been shown to reduce Cr(VI), which was not reoxidized by subsequent exposure to atmospheric oxygen over several weeks (Cai et al., 2003; Chen et al., 2003). Al(0) may be oxidized by O<sub>2</sub> and water under alkaline conditions. In the case of anaerobic conditions, hydrogen gas is produced. These reactions are likely to produce a layer of Al-(hydr)oxides on the surface of Al(0) particles and thereby diminish the reactivity of Al(0). Discrete Al(0) particles in bottom ashes have been identified with such surface layers of Al-oxides (Magel et al., 2001). Oxidation of Cr(III) by Mn-oxides is the main pathway for conversion of Cr(III) to Cr(VI) in natural systems (Barlett and James, 1979; Eary and Rai, 1987; Johnson and Xyla, 1991; Fendorf and Zasoski, 1992). However, the alkaline conditions of APC residues cause Cr(III) and Mn-oxides to occur mainly as solids, thereby decreasing the Cr(III) oxidation rates. Astrup et al. (IV) argued that Cr(III) oxidation in APC residue systems was not important.

Astrup et al. (IV) suggested that the relative importance of the following reactions controls Cr leaching in APC residue systems:



Cr(VI) is released from the residues to solution at a rate controlled by the dissolution of Cr(VI)-containing phases, e.g. Ba(S,Cr)O<sub>4</sub> or PbCrO<sub>4</sub> (Eq 1). Dissolved Cr(VI) may be reduced to Cr(III) by Al(0) (Eq 2). In the presence of dissolved oxygen Al(0) may be oxidized (Eq 3), and oxidation by water may occur at anaerobic conditions (Eq 4). Gibb's free energy of reaction for the oxidation of Al suggests that oxidation of Al(0) by O<sub>2</sub> ( $\Delta G_r^0 = -842$  kJ/mol) may



**Figure 7.** Cr release as a function of time for APC residues (dry residue, semi-dry residue and fly ash). Solution Cr concentrations are related to the amount of solid residue used in the individual experiments, i.e. mg Cr/kg residue (data from Astrup et al., IV).

be more favorable than oxidation by Cr(VI) ( $\Delta G_r^0 = -661$  kJ/mol), and that oxidation of Al(0) by water ( $\Delta G_r^0 = -456$  kJ/mol) may be the least favorable.

### 5.3 Cr leaching conceptual model

By investigating the release of Cr over time for 11 different APC residues, Astrup et al. (IV) found that the Cr release was kinetically controlled within a 168-hour experimental period and highly affected by the L/S ratio of the experiment, see examples in Figure 7.

The Cr release experiments were performed at L/S 5 and 100 l/kg on carbonated as well as non-carbonated residue samples. Cr release in batches with carbonated residues at L/S 100 l/kg showed a fast release to the solution within the first 10 hours. This was followed by a slow and moderate release during the following 50-100 hours. After 100 hours, the release was negligible. The Cr release from the non-carbonated samples at L/S 100 l/kg was qualitatively similar to the carbonated samples. At L/S 5 l/kg, the Cr release was quite different from the release observed at L/S 100 l/kg. For the non-carbonated samples, the Cr concentrations in most cases dropped rapidly 1-2 orders of magnitude within the



first 4-8 hours of water contact. After this, Cr concentrations typically increased again at a much slower rate approaching an apparently stable level towards the end of the experiment. The releases at L/S 5 l/kg for carbonated samples were in general qualitatively similar to those at L/S 100 l/kg, although the amounts of Cr leached usually were smaller.

Astrup et al., (IV) proposed the following model to describe Cr release in the investigated APC residues:

$$\frac{d[\text{Al}(0)_r]}{dt} = -k_{\text{Al-ox}}[\text{Al}(0)_r] \quad (5)$$

$$\frac{d[\text{Cr(VI)}]}{dt} = k_{\text{Cr-s}}([\text{Cr(VI)}_s] - [\text{Cr(VI)}]) - k_{\text{Cr-red}}[\text{Cr(VI)}] \cdot [\text{Al}(0)_r] \quad (6)$$

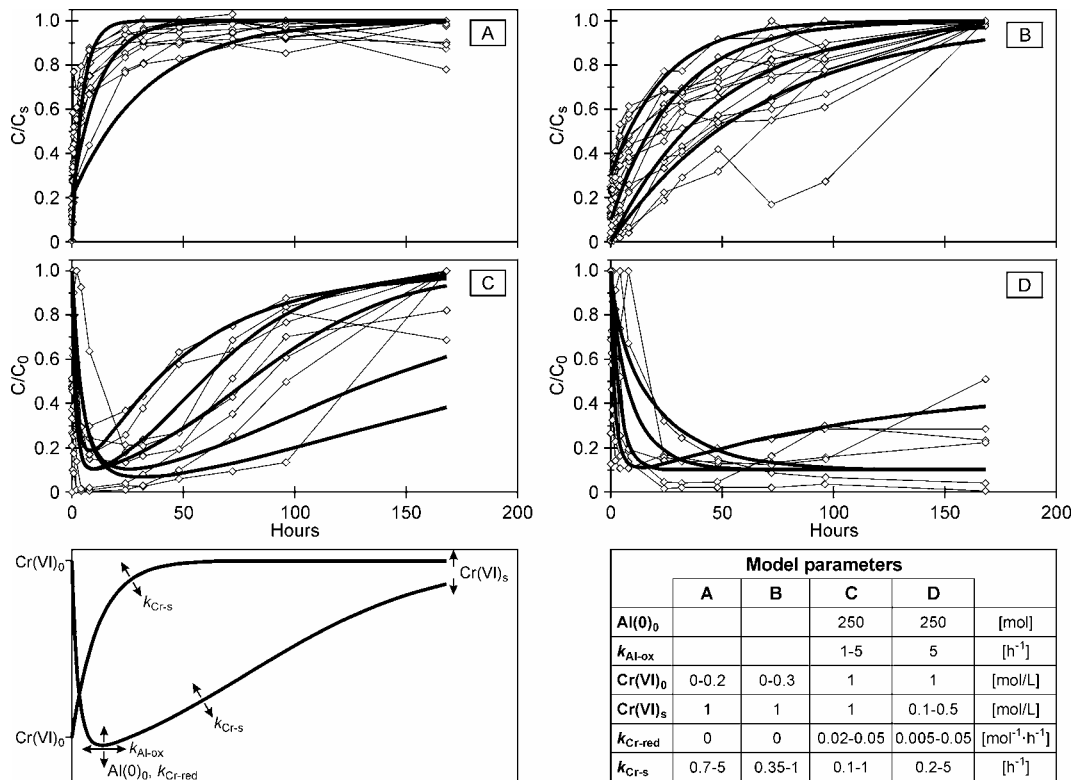
where  $\text{Al}(0)_r$  denotes  $\text{Al}(0)$  that is available for oxidation by  $\text{Cr(VI)}$  (Eq 2),  $\text{O}_2$  (Eq 3), or water (Eq 4). The associated first order rate constant is  $k_{\text{Al-ox}}$ .  $\text{Cr(VI)}_s$  is the solubility of  $\text{Cr(VI)}$ . The rate constant for  $\text{Cr(VI)}$  dissolution is  $k_{\text{Cr-s}}$ , and the rate constant for  $\text{Cr(VI)}$  reduction is  $k_{\text{Cr-red}}$ . The reduction of  $\text{Cr(VI)}$  is proposed to be second order with respect to the  $\text{Cr(VI)}$  concentration and the amount of reactive  $\text{Al}(0)_r$ .

Astrup et al. (IV) found that Cr leaching in the APC residues could be explained by varying the above rate constants, i.e. varying the relative importance of the involved reactions. Thus, Cr release at L/S 100 l/kg could be explained mainly by dissolution kinetics. The complex Cr release behavior at L/S 5 l/kg for the non-carbonated samples was explained by a combination of  $\text{Cr(VI)}$  dissolution and  $\text{Cr(VI)}$  reduction. Although significant variations in release behavior were observed among the 11 residues investigated, the Cr releases in all experiments could be explained by the above model, see Figure 8.

#### 5.4 Implications for leaching testing

The results provided by Astrup et al. (IV) demonstrate that real-life Cr leaching may be difficult to predict using batch leaching tests, and that interpretation of Cr leaching data should include possible Al-O<sub>2</sub>-Cr interactions. Test parameters such as headspace volume, L/S ratio and possibly mixing during experiment may significantly influence the Cr test result. However, also handling of the sample prior to leaching testing may be important as the degree of carbonation, and thereby pre-oxidation of  $\text{Al}(0)$ , can affect Cr leaching.

Testing of stabilized residues and comparison with similar non-stabilized residues have shown increased Cr leaching due to the stabilization. This is likely due to passivation of  $\text{Al}(0)$  during stabilization and sample handling resulting in increased Cr leaching in a subsequent leaching test. It can be realized that the Cr release from these residues in some cases may be relatively slow, indicating that retention times of a few hours in a technical scale stabilization process may not provide time enough to release the major part of Cr that is available for leaching.



**Figure 8.** Cr release curves from Astrup et al. (IV) categorized in four groups according to their release behavior. Note that the curves are normalized either relative to the to the equilibrium concentration (A and B), or to the concentration at  $t = 0$  (C and D). Group A and B illustrate experiments in which the release can be explained only by dissolution kinetics. Group C and D include experiments in which a combination of dissolution and reduction kinetics can explain the release, i.e. the initial drop in Cr concentrations observed in these two groups reflects Cr(VI) reduction by Al(0), whereas the later increase in concentrations (most significant in group C) reflects the continued effect of Cr(VI) dissolution when reduction by Al(0) is diminished.

This will leave Cr in the residues available for later leaching, for example, in a leaching test.

From a regulatory point of view, the discussions in this chapter suggest that Cr leaching determined by batch tests may have limited value as a parameter to control APC residue disposal.



## 6. Conclusions

The residues generated by cleaning the flue gas at waste incinerators contain high levels of salts and heavy metals. At a disposal site, the leachate from these air-pollution-control (APC) residues may contain concentrations significantly above background levels for many thousands of years. In order to manage these residues in a sustainable manner, it is necessary to quantify and evaluate this leaching with respect to a long-term perspective.

Characterization of leaching in long-term perspective is not possible entirely based on experimental data, however, modeling may provide means to estimate this leaching. Relating alkalinity leaching at specified pH-values to losses in residue alkalinity, it is possible by a simple mass balance approach to associate pH of a leaching system to the liquid-to-solid (L/S) ratio. This may further be combined with relationships between metal leaching and pH to provide estimated leaching as a function of L/S until depletion from the solid phase.

Most metals are affected by changes in pH of the leaching system. Due to a high buffer capacity, APC residues can maintain alkaline pH-values for L/S ratios of more than 2000 l/kg. For a typical landfill leaching scenario, this corresponds to about 100,000 years. The most important mechanism for buffer capacity depletion in APC residues are removal from the solid phase by leaching; neutralization reactions with acidic rainwater or intrinsic acid producing processes can be neglected within L/S 2000 l/kg. Uptake of atmospheric CO<sub>2</sub>, i.e. carbonation, can affect the composition of the residue buffer capacity and thereby lower pH of the leaching system, however, the same high L/S ratios are needed to reach acidic pH-values.

Soluble salts like Cl, K and Na are leached in very high concentrations within the first few L/S ratios but the concentrations are significantly decreased after L/S about 2 l/kg. This results in a significantly different leaching environment in a short-term perspective relative to a longer-term perspective after the first few L/S. Leaching characterization in a long-term perspective should consider this.

Long-term leaching of important elements other than the salts are mainly controlled by mineral solubility, although some heavy metals like Cd, Cr and V may be influenced by other mechanisms such as sorption, redox reactions or incorporation into mineral phases. For most elements, leaching for more than L/S 2000 l/kg is required to remove about 20-30 % of the solid content in the residues. Significant fractions of Ca, S and Pb (3-23 %) are leached within the first L/S 10

l/kg. At L/S 500 l/kg, the leached fractions of Al, Ba, Mg and V are in the order of 1-12 %. Less than 1 % of the heavy metals Cd, Ni and Zn are leached within L/S 500 l/kg. Of these elements, only Al, Mg and Zn are predicted to have higher leachate concentrations within L/S 5000 l/kg, than what may be found in an L/S 2 or L/S 10 batch test. Leachate concentrations of the other elements either remain at levels similar to the initial leachate or likely decrease to significantly lower levels. Carbonation caused increased concentrations of Ca and S only.

Cr leaching as determined by batch experiments is highly affected by the redox conditions of the test and reaction kinetics. Cr(VI) reduction capacity provided by Al(0) present in the residues may significantly lower Cr concentrations within a few hours, whereas Cr(VI) dissolution may require a day to complete. Al-O<sub>2</sub>-Cr interactions appear to control the release of Cr in batch experiments. In this respect, carbonation has an effect as Al(0) is oxidized by O<sub>2</sub> during carbonation.

The above findings may have important implications for performing leaching tests on APC residues and subsequently interpreting the data with respect to real-life leaching scenarios.

- High L/S ratios are required to reach low pH-values, whereas salt concentrations are significantly lowered within a few L/S. The relatively high salt concentrations in typical pH dependence tests at L/S 10 l/kg are not likely to be relevant at pH-values below the natural pH of the residue.
- Ca, Cd, Ni, S and Zn may all be depleted from the solid phase above pH 7 (most significant for Ca and S, which may be depleted at pH 10-11 in the case of non-carbonated residues). Thus, detailed conclusions concerning leaching at acidic pH-values may have limited value for these elements with respect to actual leaching systems.
- Cr release in batch experiments are highly affected by L/S ratio, headspace volume, experiment time and prior sample handling. Cr solution concentrations in batch leaching experiments may thus be difficult to relate to actual leaching.

## 7. Future Work

The work included in this thesis provides a basis for continued investigation within the following topics.

- **Prediction of leachate concentrations using geochemical modeling.** So far, geochemical modeling has mainly been used for assessing leaching control. A goal is however to use modeling for predicting leachate concentrations both in leaching tests experiments and in real-life leaching systems. This involves that the residues are represented in the model by a number of solid phases that account for relevant dissolution, sorption and redox reactions. In order to obtain a reasonable prediction of experimental data, the underlying mechanisms controlling leaching should be well known. This thesis provides a basis for selecting solubility-controlling minerals and for understanding Cr leaching control. The next step is to use this information in geochemical models to simulate progressive leaching and to validate the models with respect to experimental data.
- **Characterization of flow patterns in residues landfills.** Evaluation of APC residue leaching data has been done primarily based on assumptions of homogeneous flow and local equilibrium. These assumptions however need to be verified in both a short-term and a long-term perspective. Especially the importance of physical non-equilibrium should be evaluated with respect to geochemical leaching prediction.
- **Environmental impact assessment.** The temporal variations in residue leaching illustrated in this thesis are generally not accounted for in present impact assessment models (Hellweg, 2000). Typically, impacts are categorized with respect to a short-term period and a long-term period. Flexible methods for including these temporal changes in leachate concentrations should be developed.
- **Estimation of Cr leaching.** In order to model Cr leaching in detail, further evaluation of the Al-O<sub>2</sub>-Cr system should be performed. Especially, the possible influence from pH changes on Cr(VI) reduction by Al(0) in residue systems needs to be addressed, and the Al-O<sub>2</sub>-Cr interactions should be evaluated with respect to column leaching experiments.



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